STUDIES IN THE AROMATIC POLYCYCLIC SERIES

by

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in the Faculty of Science.

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CONTENTS

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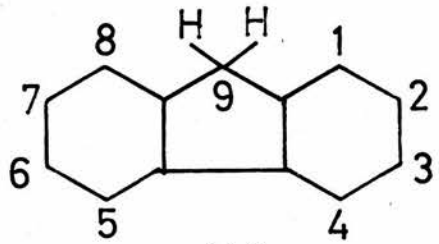
Experimental Results.

Nomenclature

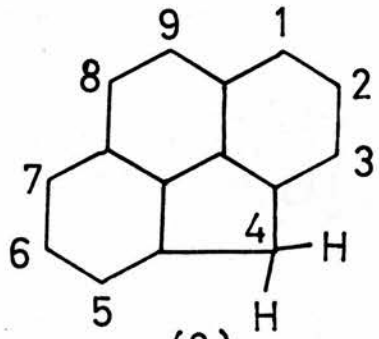
Five polynuclear aromatic hydrocarbon systems are involved in this thesis. The names and numbering of these hydrocarbons employed are shown below.

Fluorene (1)



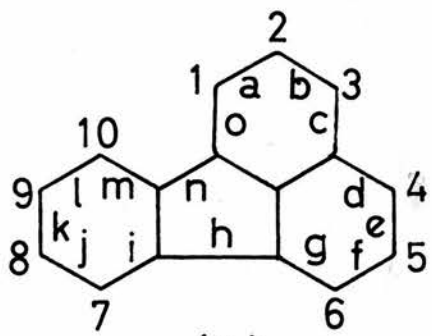
(1)

4H-cyclopenta(def)phenanthrene (2)



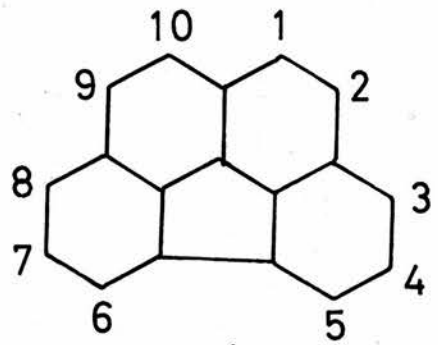
(2)

Fluoranthene (3)



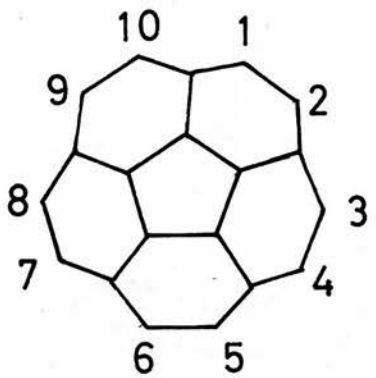
(3)

Benzo(ghi)fluoranthene (4)



(4)

Coronindene (5)

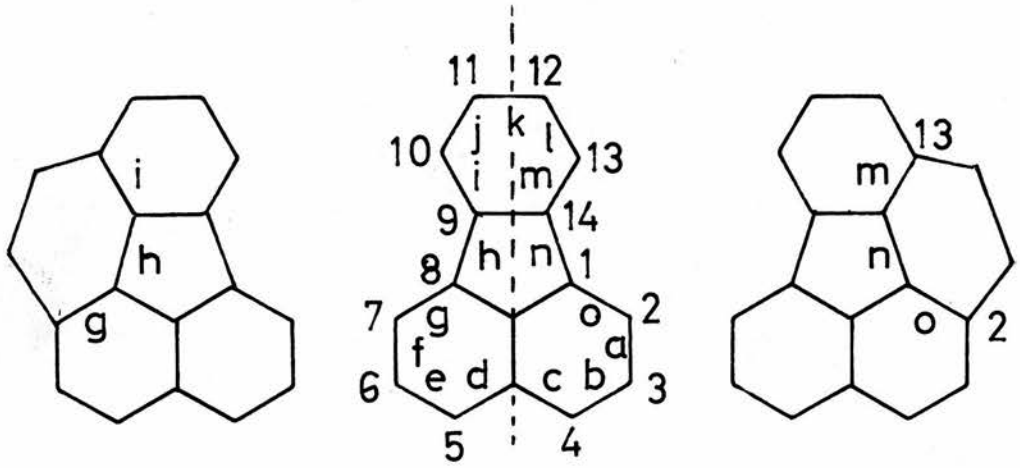


(5)

Some confusion may arise over the naming of the benzofluoranthene 4. This compound was first reported [1] as benzo(mno)fluoranthene, this name being retained by Clar [2], who also named it 2:13-benzofluoranthene. Benzo(ghi)fluoranthene, the name employed in this thesis, is that used by Chemical Abstracts. These various names arise as follows.

The old system of numbering fluoranthene is shown below, and from this can be seen the synonymous naming

of 2:13benzofluoranthene and benzo(mno)fluoranthene.



Due to the symmetry of fluoranthene, as shown by the dotted line, the equivalence of the lettering (ghi) and (mno) becomes apparent, the former being preferred, as it involves letters occurring earlier in the alphabet.

SECTION I

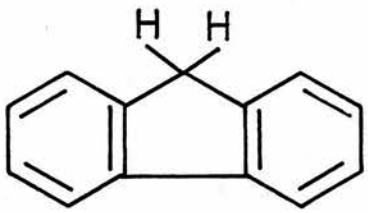
Attempted Synthesis of Coronindene

Introduction

Part 1.

A brief introduction to these aromatic systems is necessary before embarking on the discussion of the work of this section proper.

Fluorene



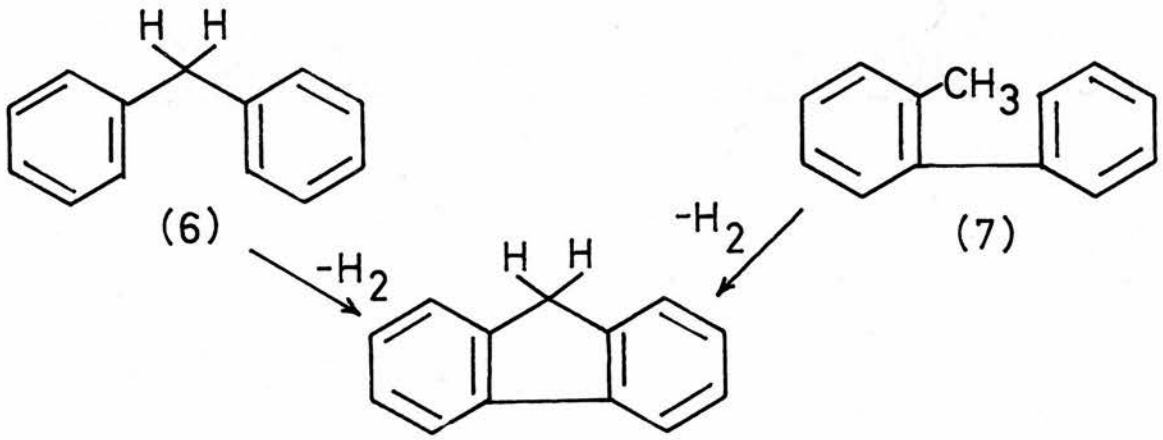
(1)

Throughout the whole of the work reported in this thesis, the hydrocarbon fluorene (1) figures very prominently. With two exceptions - cyclisations to the corresponding fluoranthenes - all the reactions discussed involve the 9-methylene position and 9-substituted fluorene derivatives. The brief summary of fluorene which follows thus concentrates more on reactions involving this aspect of fluorene chemistry, and less on the aromatic substitution reactions.

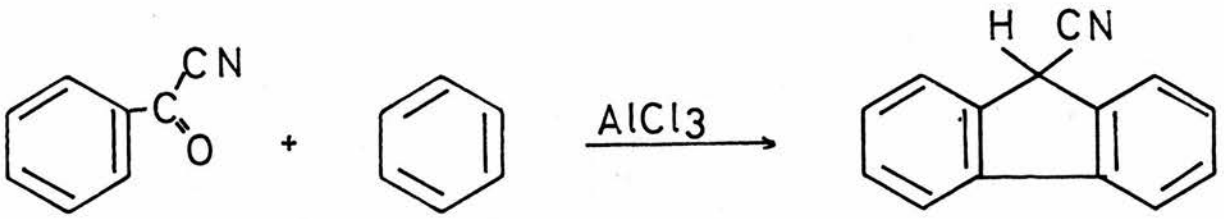
Structure. First isolated in 1867 by Berthelot [3], the structure of fluorene had been established [4,5] through chemical methods by 1878 as diphenylenemethane (1). Recent detailed X-ray analysis [6,7] has clarified the stereochemistry, showing that, at least in the solid

state, fluorene is a planar molecule. Strain is accommodated by abnormal bond lengths and angles, and not by the planes of the six-membered rings being inclined to that of the five-membered ring as previously reported [8].

Syntheses. There are many synthetic methods of preparing fluorene and its derivatives, the latter either from the appropriate substituted starting materials, or by substitution of the fluorene nucleus. Fluorene has been prepared by methods which well illustrate its structure. The catalytic cyclodehydrogenation at high temperature of diphenylmethane (6)[9] and 2-methyldiphenyl (7)[10] give fluorene.

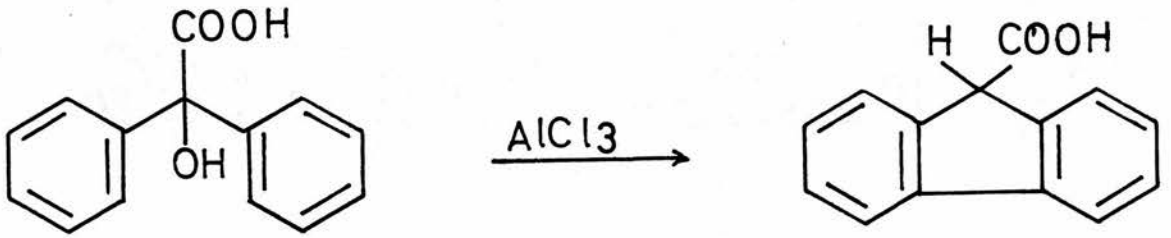


Dehydration of appropriate compounds can lead to fluorene. Thus, interaction between benzoyl cyanide (9) and benzene (8), with aluminium chloride as catalyst, gave [12] 9-cyanofluorene (10).



(9) (8) (10)

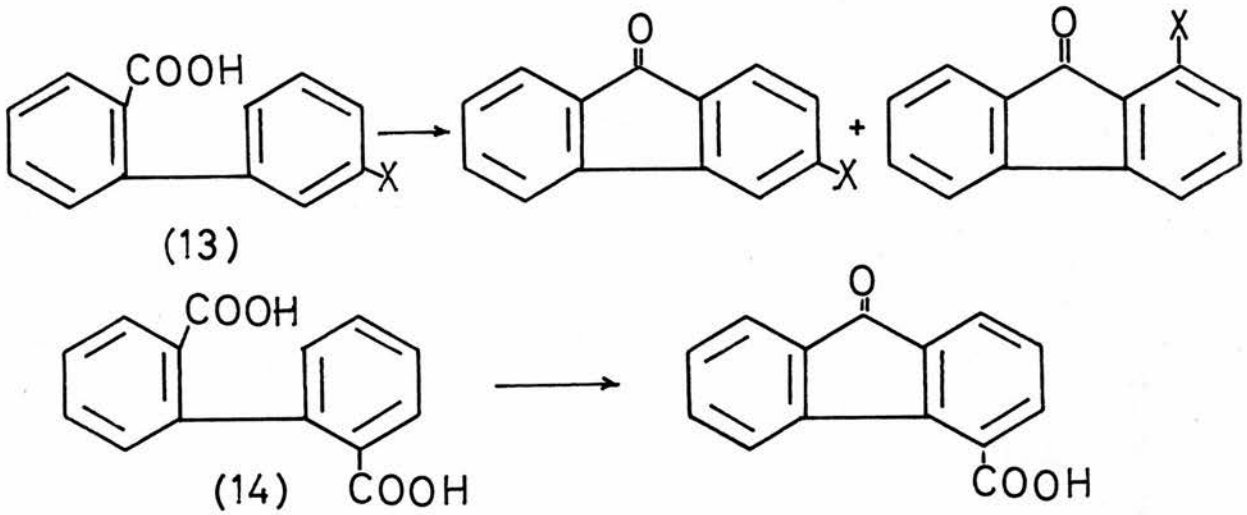
A similar reaction with benzilic acid (11) gave fluorene-9-carboxylic acid (12).



(11) (12)

Dehydration reactions leading to fluorenones have often been employed in the synthesis of fluorenes, the subsequent reductions being achieved by zinc dust distillation, boiling with phosphorus and hydriodic acid, or by heating to a high temperature with hydrazine hydrate. Sulphuric acid cyclodehydration [13,14] of diphenyl-2-carboxylic

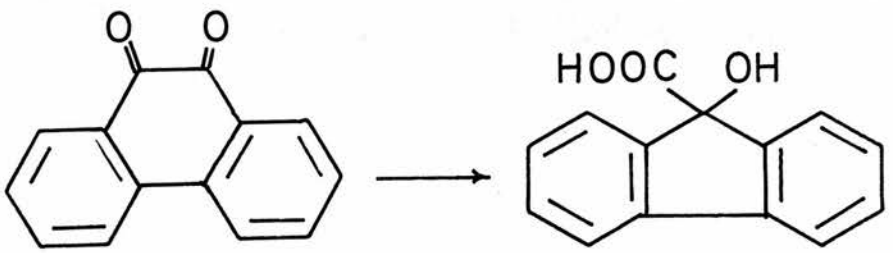
acids (13) or diphenic acid (14) gives fluorenones.



(13)

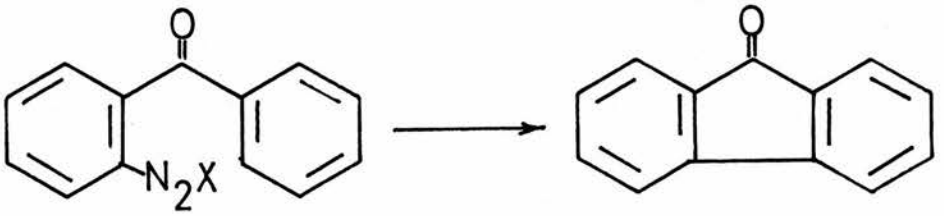
(14)

A benzilic acid type rearrangement of phenanthraquinones with base furnishes a synthesis of fluoren-9-ol-9-carboxylic acids(15) which are readily oxidised to the fluorenones [15].



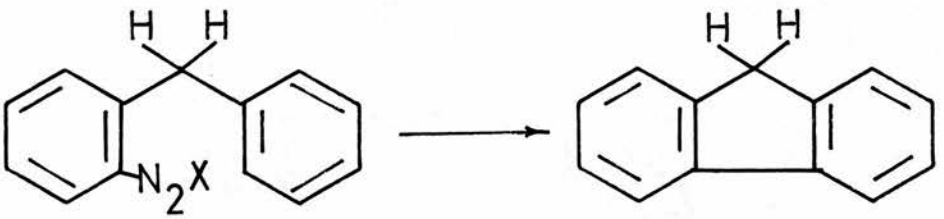
(15)

The coupling of diazotised 2-aminobenzophenones (16) has given rise to fluorenones [16].



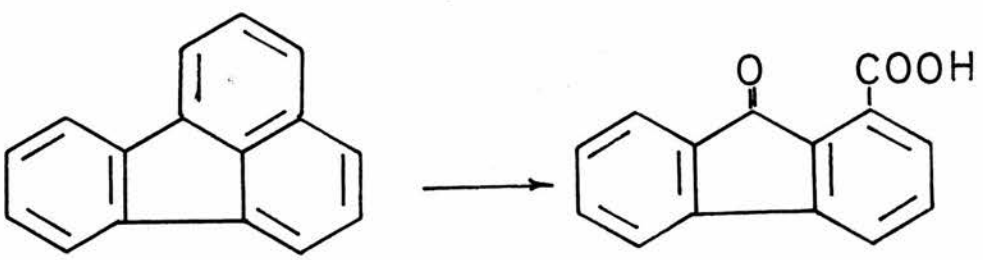
(16)

The analogous reaction with 2-aminodiphenylmethanes (17) affords fluorene directly.



(17)

Oxidation of fluoranthene (3) by chromic acid gives fluorenone-1-carboxylic acid (18)[17]. A number of fluorenones have been prepared by this method.



(3) (18)

Substituted fluorenes can be prepared by direct substitution of the nucleus (see below).

Reactions of Fluorene.

The reactions of fluorene fall into two distinct classes, viz. those involving the aromatic nucleus, and those involving the aliphatic 9-position.

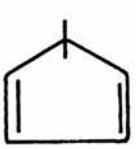
Nuclear Substitution.

Substitution by electrophilic reagents involves primarily the 2-position, further substitution mostly occurring at the 7-position [18,19]. In addition, with an electron-attracting group in the 2-position, some disubstitution may also occur in the 5-position; an electron-releasing group tending also to effect some disubstitution at the 3- and 1-positions. The nature of a substituent at the 9-position of fluorene has no effect on the orientation of nuclear substitution. The converse, however, does not hold, nuclear substituents influencing the reactivity of the methylene group [20,21].

Reactivity of the 9-methylene position.

Cyclopentadiene (19), indene (20), fluorene (1), and 4H-cyclopenta(def)phenanthrene (2), can be regarded as a series, having in common the basic conjugated structure of

the first named of these compounds.



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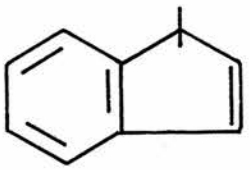

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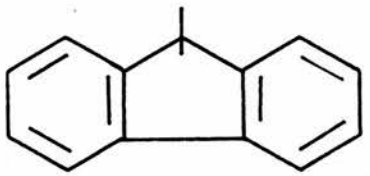
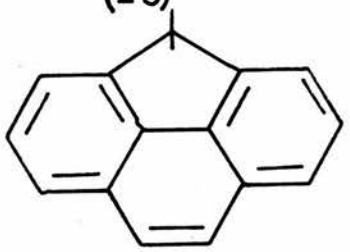
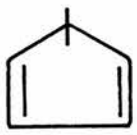


(1)



(2)

Methylene groups situated between two double bonds in this manner are activated, in as much as the hydrogen atoms are readily lost as protons, the resultant carbanion being stabilised by delocalisation. This reactivity decreases in the order cyclopentadiene > indene > fluorene ≥ 4H-cyclopenta-(def)phenanthrene. This decrease is probably due to the decrease in double-bond character of the five-membered ring on annealation of the delocalised aromatic nuclei.



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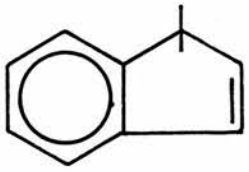

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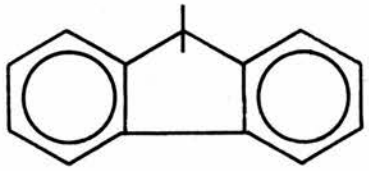
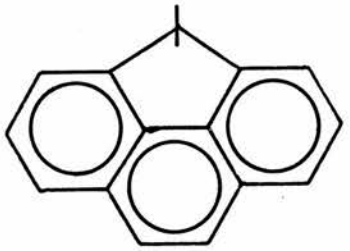


(1)



(2)

This reactivity is reflected in the ability of all of these compounds to form alkali-metal derivatives, and in their acidity measurements. Experimentally derived [22,23] pK values for these compounds agree with the chemically experienced order of reactivity.

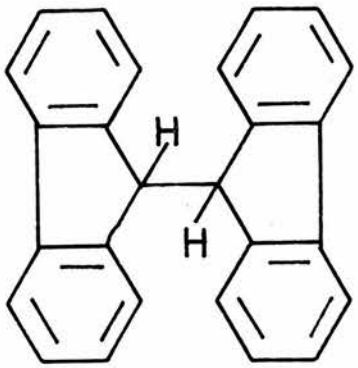
Compound	pK
cyclopentadiene	16
indene	21
fluorene	25
4H-cyclopenta(def)phenanthrene	31

In the case of fluorene, this reactivity of the methylene group is illustrated by the following reactions, many of which were employed in the course of the work embodied in this thesis.

The sodium [24], potassium [25], and lithium derivatives can be prepared, the last mentioned very readily by the displacement of the metal from the less acidic butyl- or phenyl- lithium [26]. A similar displacement reaction is the formation [27], from ethylmagnesium bromide, of 9-fluorenyl-magnesium bromide, a useful Grignard reagent.

Dehydrogenation by heating fluorene with lead oxide, results in loss of the reactive methylene hydrogens, coupled with dimerisation, leading first to the colourless

bifluorenyl (21) and then to the deep red bifluorenylidene (22)[28].



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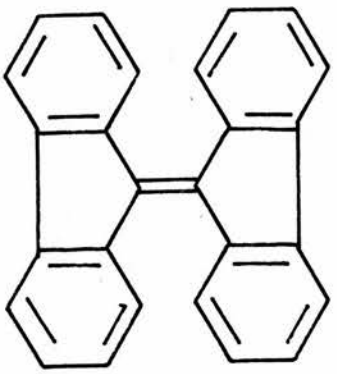
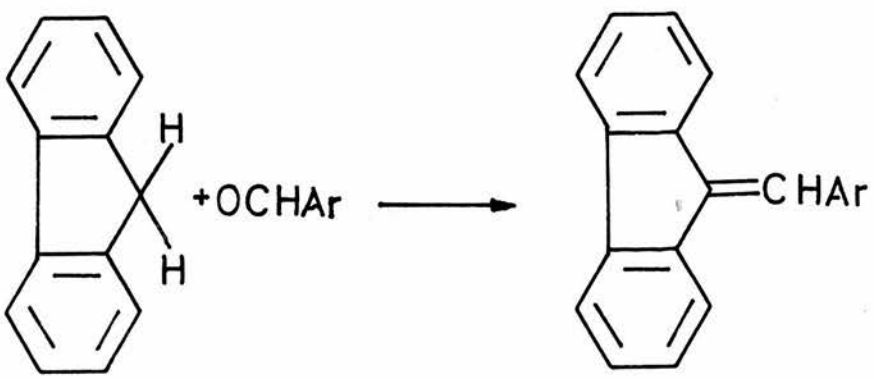


(22)

Irradiation of fluorene and bromine in carbon tetrachloride leads to the formation of the 9-bromo- and 9:9-dibromo- derivatives [29], the former being more readily obtained by bromination with N-bromosuccinimide [30].

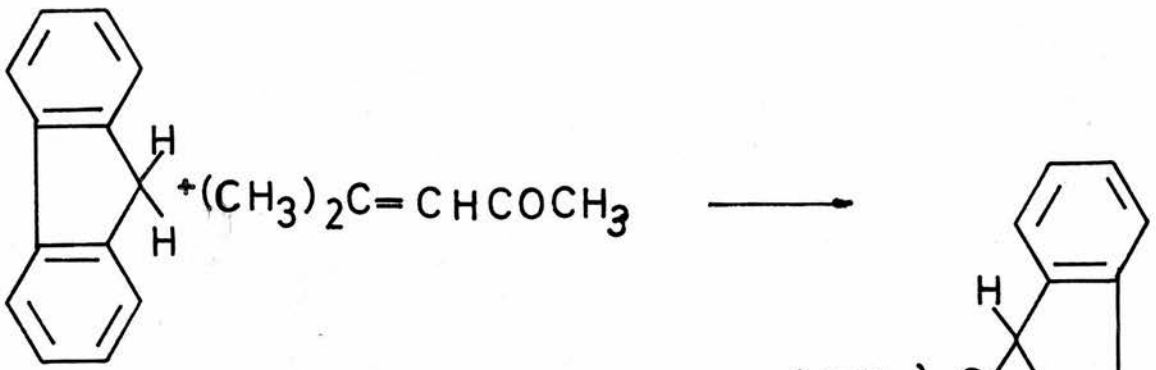
Due to the acidity of the methylene group, fluorene undergoes many base-catalysed reactions. When heated with potassium hydroxide and benzyl chloride, fluorene gives 9:9-dibenzylfluorene. Fluorene condenses with aromatic aldehydes in the presence of sodium alkoxide to give 9-arylidenefluorenes (23)[31].



(23)

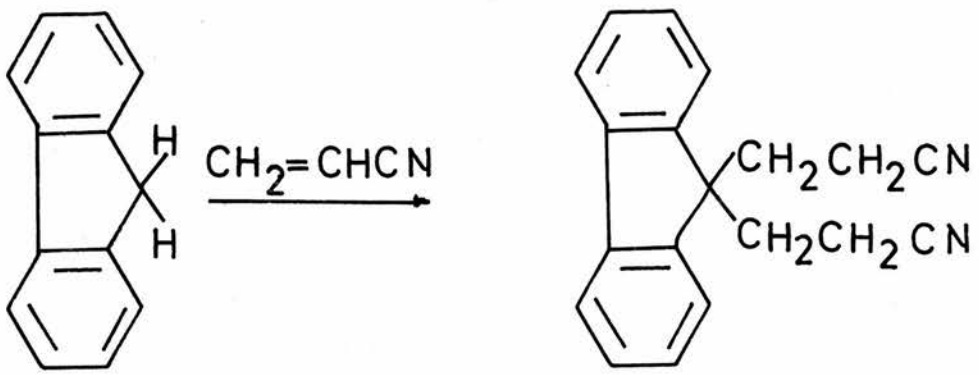
A few cases of analogous condensations with aliphatic aldehydes have also been observed, e.g., n-butylidenefluorene[32].

Fluorene does not condense with saturated ketones. Acetone, however, undergoes self-condensation to form mesityl oxide, which combines with fluorene, by a Michael reaction, to give methyl-β-9-fluorenyl-β-methyl-n-propyl ketone (24)[33].

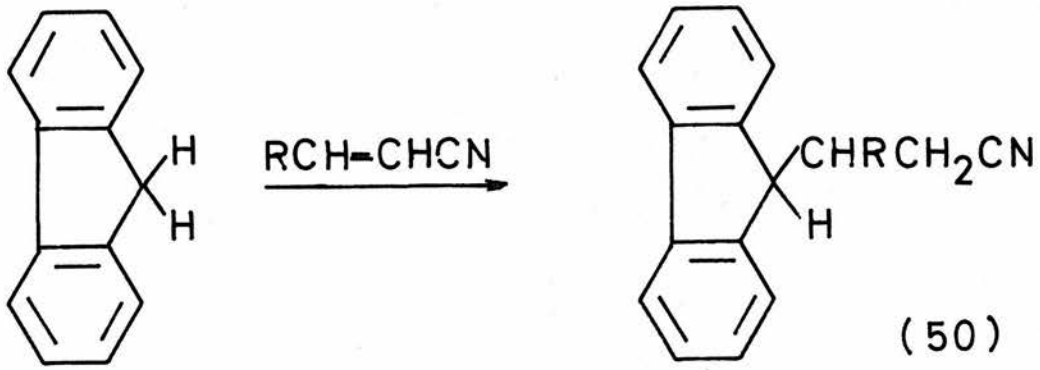


(24)

Fluorene readily undergoes such Michael reactions, indeed it is difficult, if not impossible, to prevent two molecules of acrylonitrile adding to one molecule of fluorene [34], except by having one 9-substituent already present, e.g., carboethoxy or hydroxy.

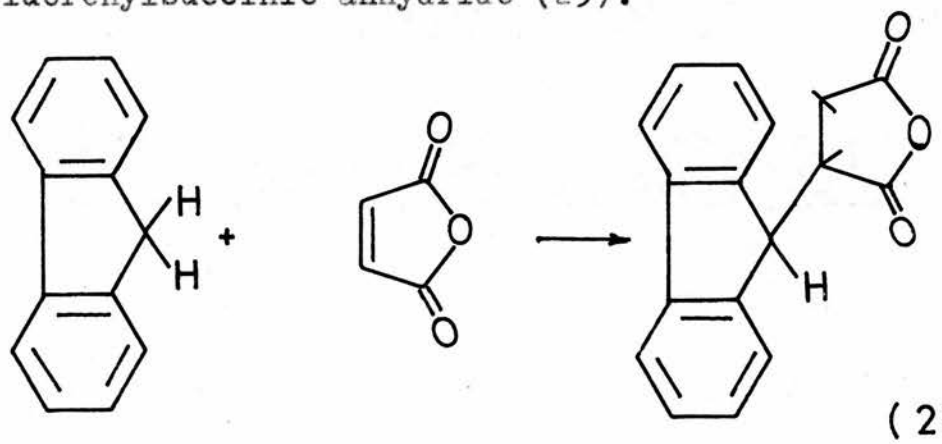


Crotononitrile [34] ($R=CH_3$) and Cinnamonitrile [35] (R=Ph), however, only add in equimolar proportions, the former to give β-methyl-β-9-fluorenyl propionitrile (50 R=Me).



(50)

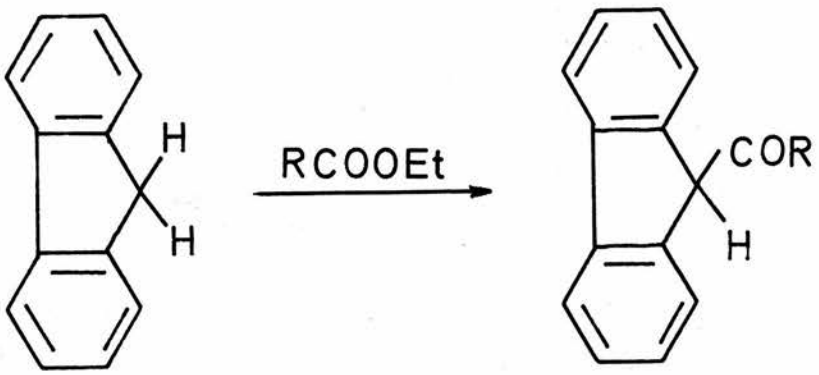
Fluorene reacts with maleic anhydride to form 9-fluorenylsuccinic anhydride (25).



(25)

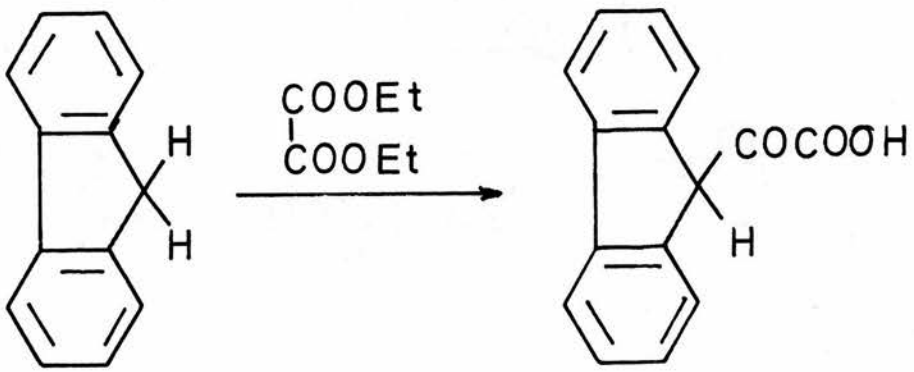
The last three examples above can lead to fluoranthene derivatives by hydrolysis and cyclisation.

A further base-catalysed reaction of the 9-methylene group is a Claisen type condensation with esters. With ethyl formate fluorene gives 9-formylfluorene (26 R=H) and with ethyl acetate, 9-acetylfluorene (26 R=Me) [36].



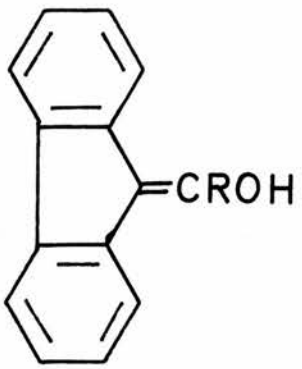
(26)

Condensation with ethyl oxalate gives, after hydrolysis, 9-fluorenylglyoxalic acid (27)[37].



(27)

Due to the acidity of the 9-hydrogen atom in fluorene derivatives, considerable enolisation occurs, the enol forms tending to predominate through stabilisation by their greater degree of conjugation. Both 9-formylfluorene (28 R=H) and 9-acetylfluorene (28 R=Me) have been shown [38, 36] to exist in the enol form, as also does 9-fluorenylglyoxalic acid (29)[39].



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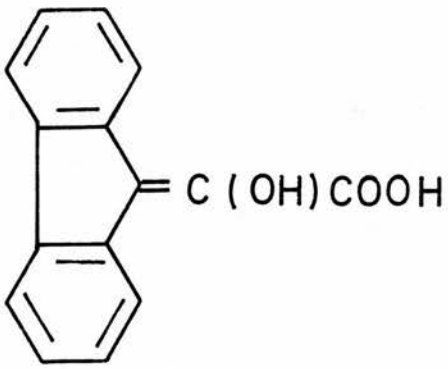
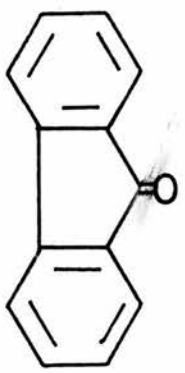


(29)

The methylene group is readily oxidised, by sodium dichromate in boiling acetic acid, to the corresponding ketone, fluorenone (30). This compound is useful synthetically, especially in its reactions with Grignard reagents.



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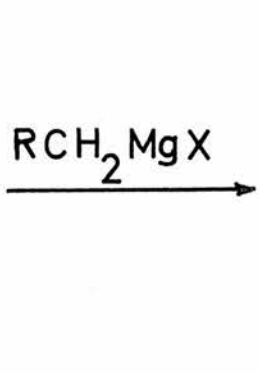
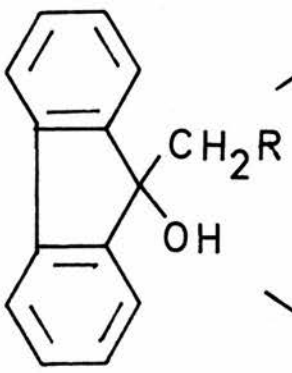
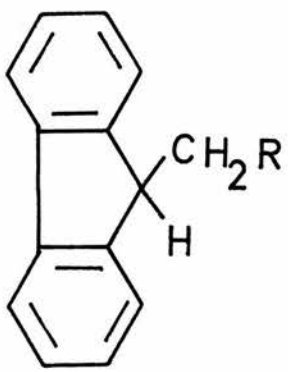
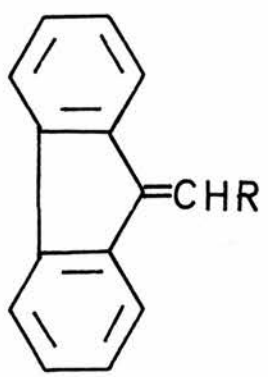




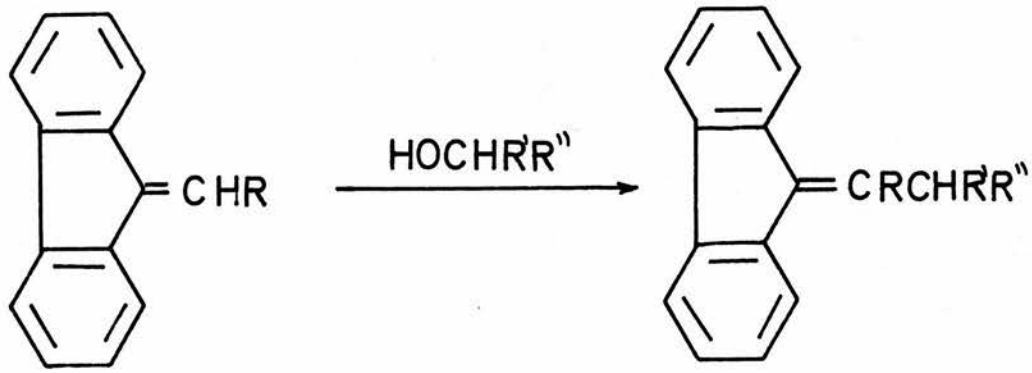
(31)





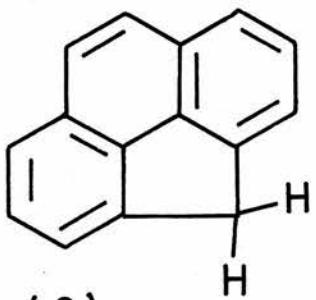
(32)

Such 9-fluorenylidene compounds as 32, from dehydration of the 9-alkyl-9-fluorenol 31, undergo a further interesting dehydration with carbinols to give extended 9-fluorenylidene compounds [40,41].



4H-cyclopenta(def)phenanthrene.

Structure.

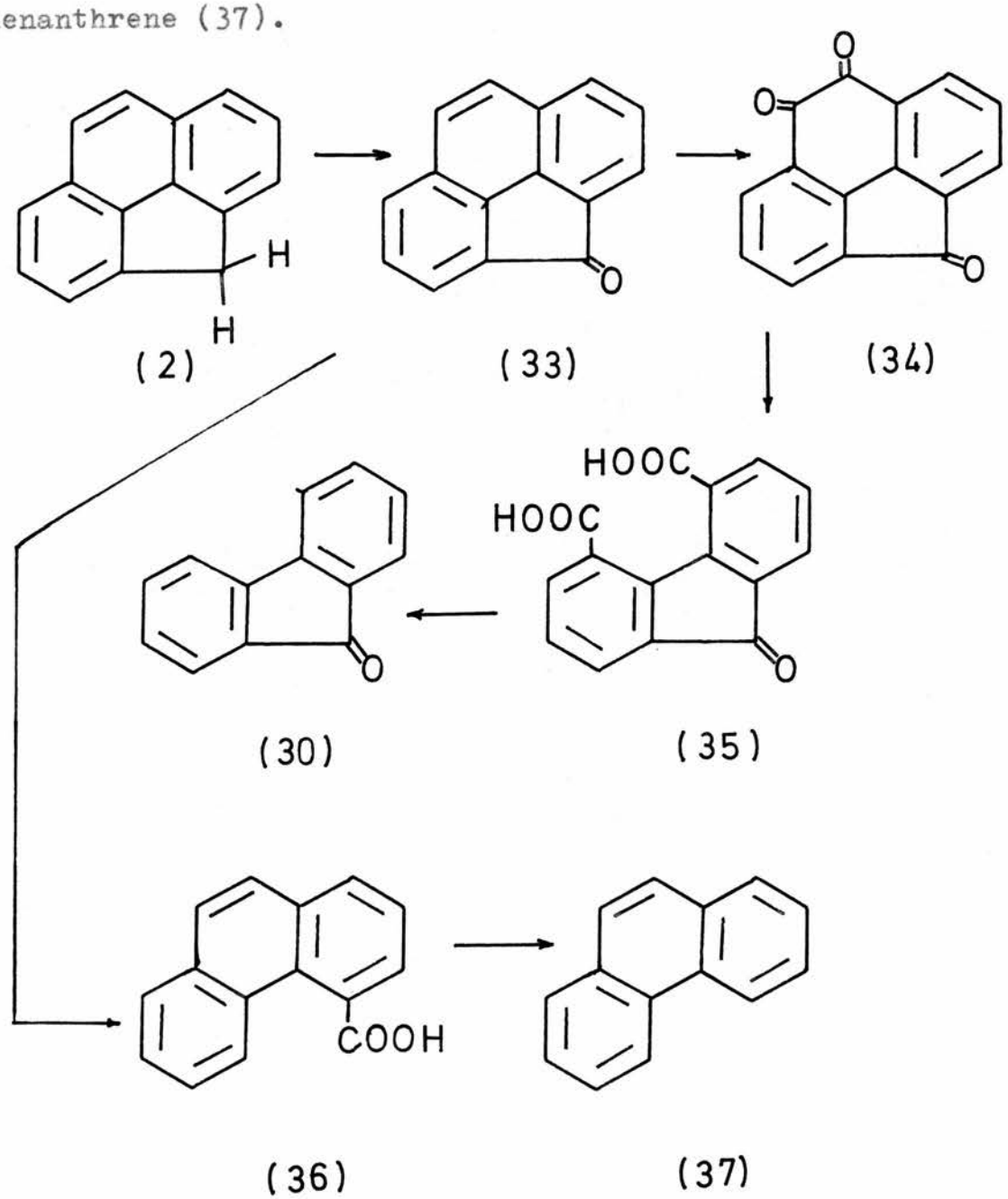


(2)

This compound was first isolated in 1934 [42] by treatment of the crude anthracene oil fraction (b.p. 350°-360°) with sodium, which formed the 4-sodio derivative. Treatment of this with carbon dioxide, followed by acidification and decarboxylation, gave the hydrocarbon 2.

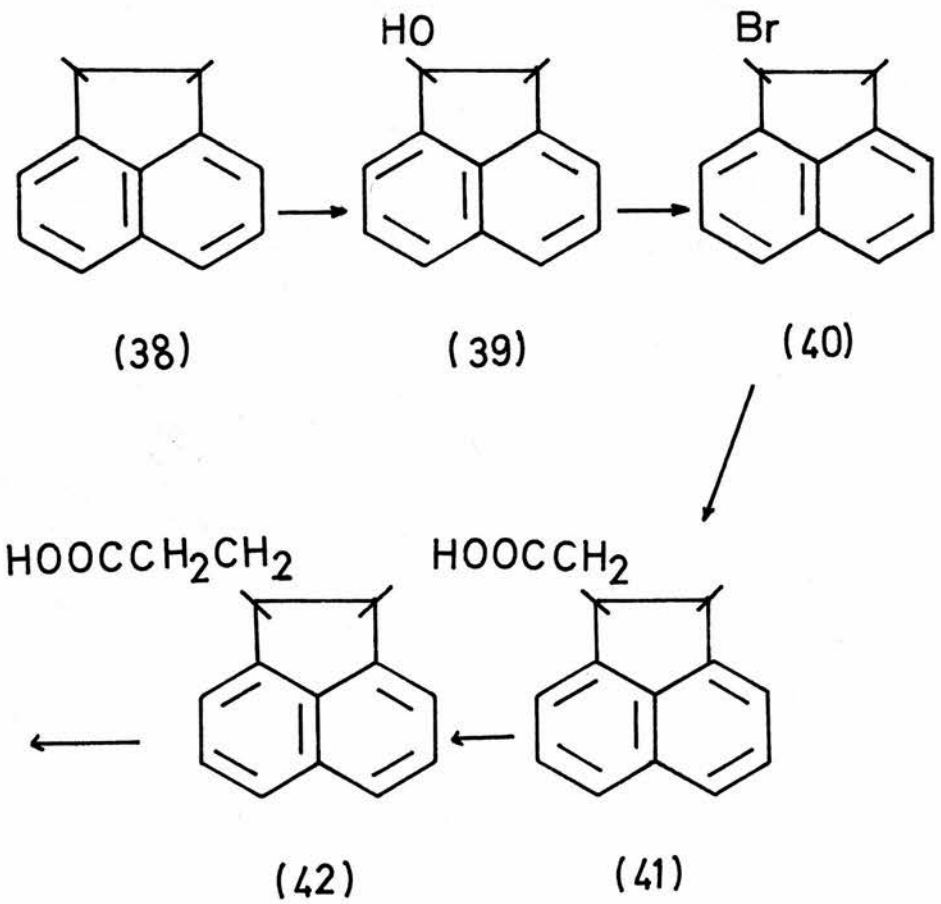
The structure was established by oxidative degradation which illustrated its relationship to fluorene (1) and phenanthrene (37). Mild oxidation afforded the

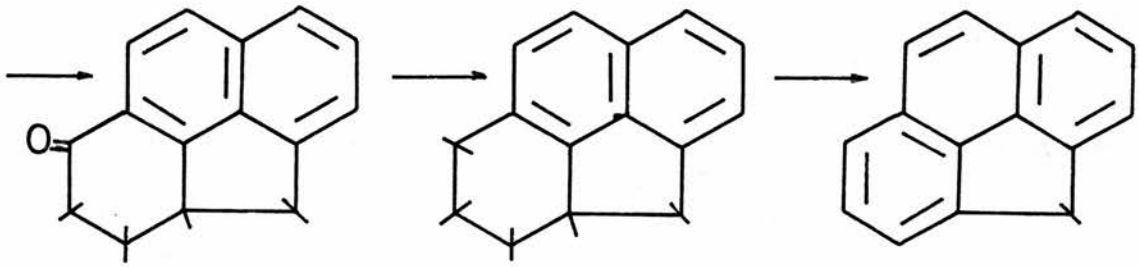
4-keto-derivative 33 which, on more vigorous treatment gives first 4-keto-4H-cyclopenta(def)phenanthra-8:9-quinone(34), and then 9-fluorenone-4:5-dicarboxylic acid (35). The latter was decarboxylated to fluorenone (30). Alkali fusion of 33 yielded phenanthrene-4-carboxylic acid (36) which decarboxylated to phenanthrene (37).



(2) (33) (34) (30) (35) (36) (37)

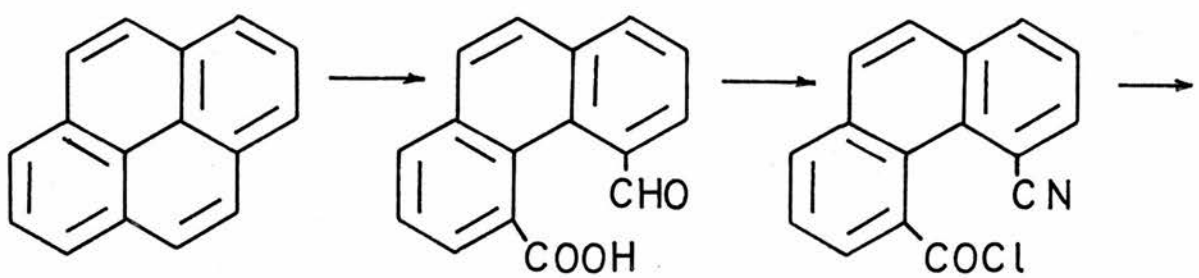
Syntheses. The structure was confirmed by synthesis [43]. Acenaphthylene (38), on treatment with lead tetra-acetate, gave the 1-acetyl derivative which hydrolysed to 1-acenaphthol (39). This was converted into the bromide 40, which condensed with malonic ester to give, after hydrolysis and decarboxylation, 1-acenaphthenylacetic acid (41). The Arndt-Eistert reaction chain-extended this acetic acid to 1-acenaphthenylpropionic acid (42), which, on cyclisation, afforded 7-keto-4a:5:6:7-tetrahydro-4H-cyclopenta(def)phenanthrene (43). Reduction to 4a:5:6:7-tetrahydro-4H-cyclopenta(def)phenanthrene (44), followed by dehydrogenation, gave the hydrocarbon 2.



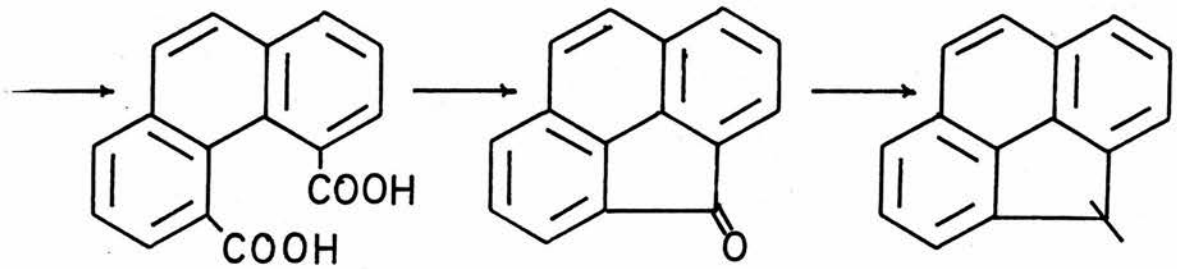


(43) (44) (2)

A second synthesis [44] involves the reduction in size of one of the rings in the pyrene (45) molecule. Ozonolysis of pyrene (45) gave 4-carboxy-5-phenanthrene-aldehyde (46), which was converted into the oxime. Dehydration with thionyl chloride afforded 5-cyanophenanthrene-4-carboxylic acid chloride (47), hydrolysis of which gave phenanthrene-4:5-dicarboxylic acid (48). Dry distillation of the barium salt gave 4-keto-4H-cyclopenta(def)phenanthrene (33), which was reduced to the hydrocarbon 2.



(45) (46) (47)



(48) (33) (2)

Nuclear substituted 4H-cyclopenta(def)phenanthrenes are known, prepared either by starting with a substituted acenaphthylene in the first of the above syntheses, by Grignard reactions on the cyclic ketones formed in this synthesis, or by reduction of the ketones formed by Friedel-Crafts reactions with acetyl chloride.

The substitution reactions of 4H-cyclopenta(def) phenanthrene are not involved in this present work, and mention is only made of this Friedel-Crafts acetylation, which substitutes in the 1- and 3-positions [43].

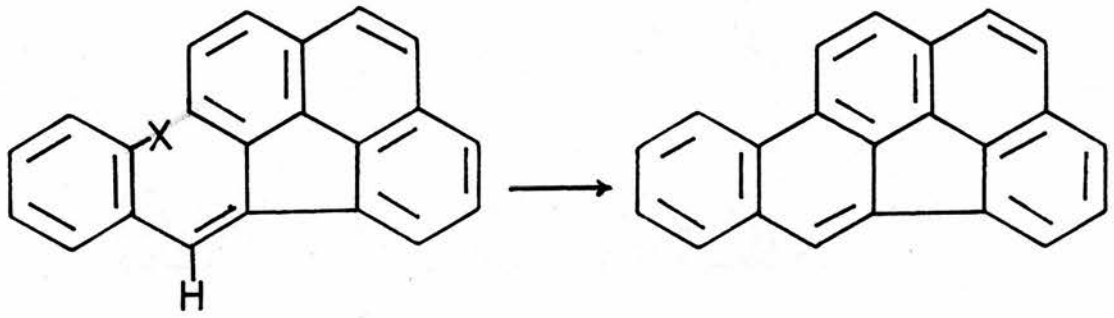
Reactivity of the methylene group.

The work described in this section of the thesis involves the reactivity of the methylene positions of 4H-cyclopenta(def)phenanthrene and fluorene. The acidities of these compounds have already been discussed

and, as with fluorene, some examples are given to illustrate the reactivity of the cyclopentaphenanthrene.

The formation of the 4-sodio-derivative described in the isolation of the hydrocarbon indicates the acidity of the methylene group. Like fluorene, 4H-cyclopenta(def)phenanthrene condenses [42] with aromatic aldehydes to give benzylidene derivatives (49).

Campbell and Reid [1] effected the condensation of 4H-cyclopenta(def)phenanthrene and o-chloro- and o-bromo-benzaldehyde, cyclisation of the products giving dibenzo-(b, ghi)fluoranthene (50).

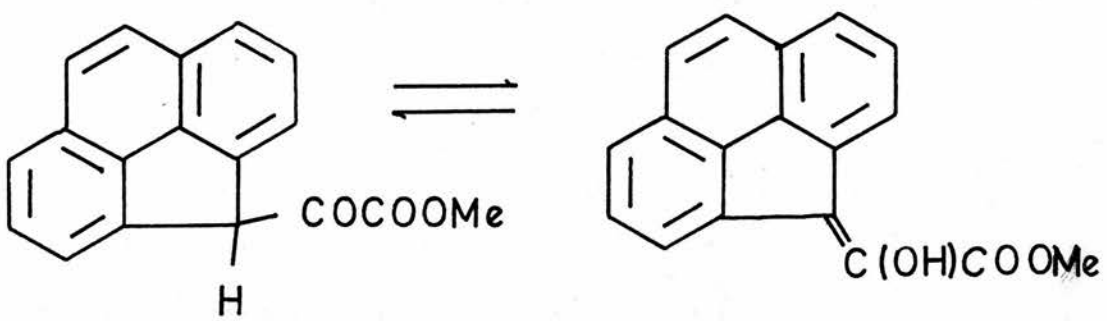


(49) (50)

4H-cyclopenta(def)phenanthrene undergoes Michael addition with activated double bonds, adding, like fluorene, two molecules of acrylonitrile [45]. Evidence of a lesser activity of the methylene group in 4H-cyclopenta(def)phenanthrene as compared with fluorene, indicated in the pK values (p.11), can be drawn from the fact that no addition was obtained with 4H-cyclopenta(def)phenanthrene and cinnamonitrile [45]

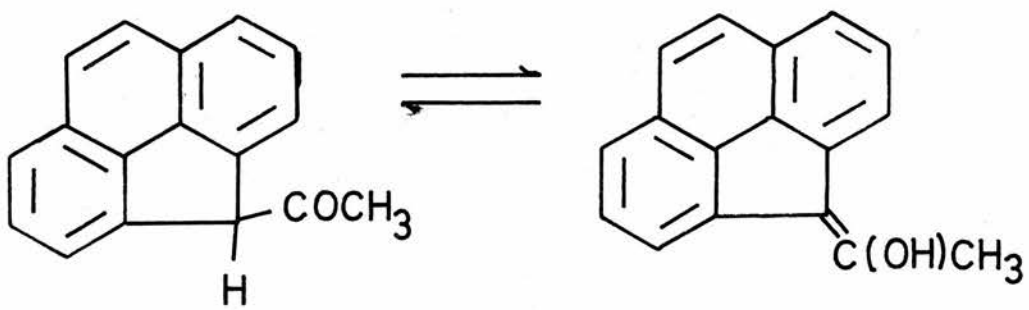
or crotononitrile (p.59), although such condensations do take place with fluorene [34,35].

In a Claisen type reaction, 4H-cyclopenta(def)phenanthrene reacts, as does fluorene, with dimethyl oxalate to give methyl-4H-cyclopenta(def)phenanthrene-4-glyoxalate, which exists in both the keto (51) and enol (52) forms [47].



(51) (52)

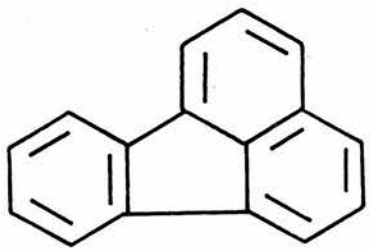
An analogous reaction is the condensation with ethyl acetate, the 4-acetyl-4H-cyclopenta(def)phenanthrene also existing in a keto (53)-enol (54) equilibrium [48].



(53) (54)

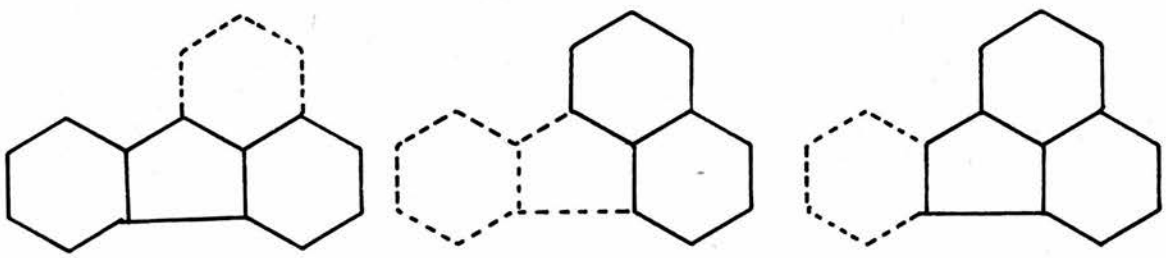
From the above résumés, the analogous behaviour of the methylene groups of fluorene and 4H-cyclopenta(def)phenanthrene are demonstrated.

Fluoranthene.



(3)

Fluoranthene itself features only briefly in this thesis, and the fluoranthene system is accorded only slight attention in this introduction. Although the hydrocarbon was isolated [49] in 1877, the correct structure was assigned [50] only in 1929. Fluoranthene may be regarded as embodying the systems of fluorene (A), naphthalene (B), and acenaphthene (C).

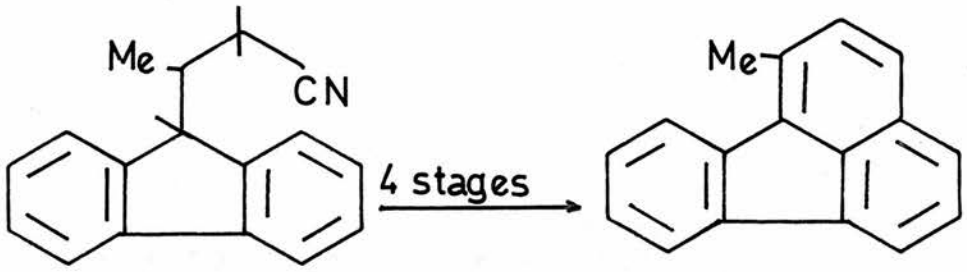


(A) (B) (C)

These relationships are reflected in the three main synthetic routes to fluoranthenes, that appertaining to fluorene being of particular relevance to the present work.

Syntheses.

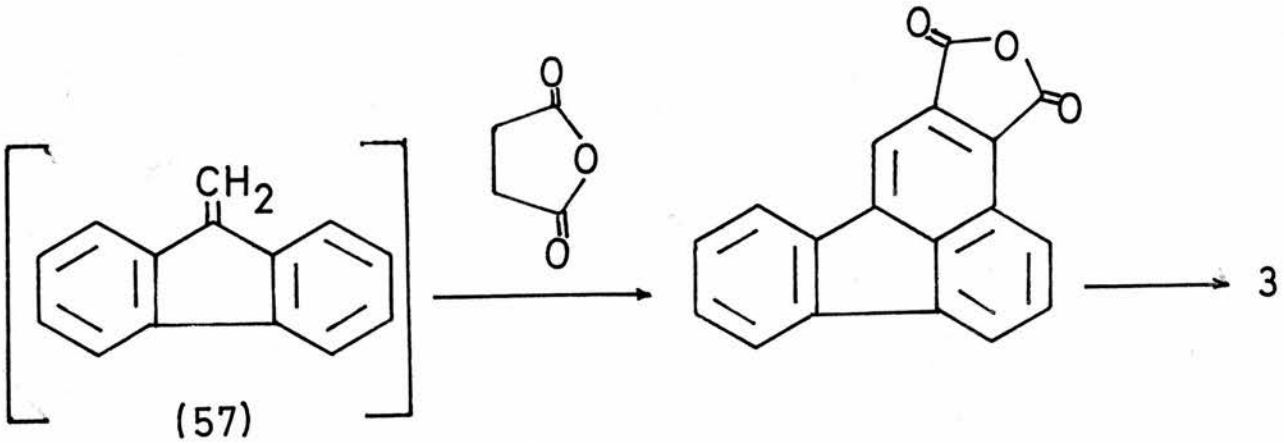
A. From fluorene. Fluoranthenes have been synthesised by cyclisation of the appropriate fluorene-9-propionic acid. The previously mentioned (p.14) β-methyl- β-9-fluorenyl propionitrile (55) on hydrolysis, cyclisation, reduction, and hydrogenation gives [37] 1-methylfluoranthene (56).



(55) (56)

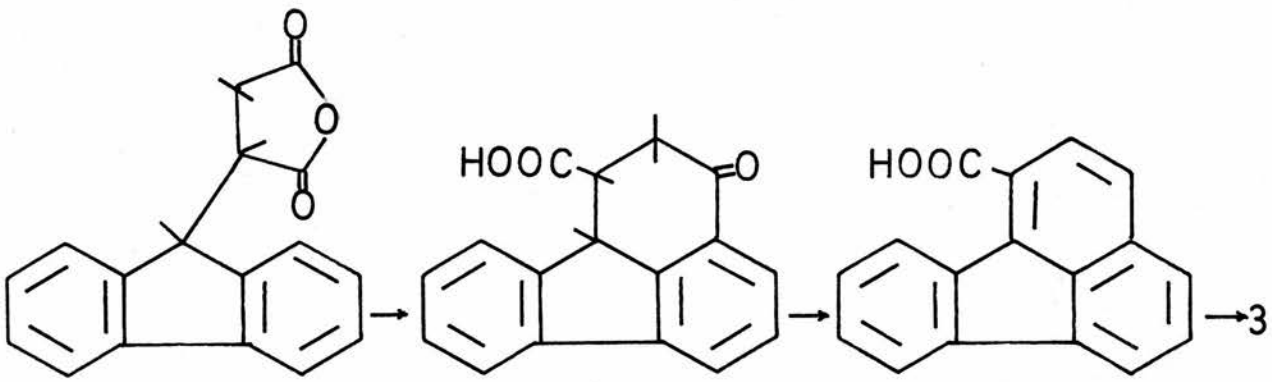
Similarly, 2-methylacrylonitrile was employed [51] in the synthesis of 2-methylfluoranthene.

An intermediate subsequently utilised in this work, 9-methylenefluorene (57), provides a route to fluoranthene by a Diels-Alder addition with maleic anhydride [52].



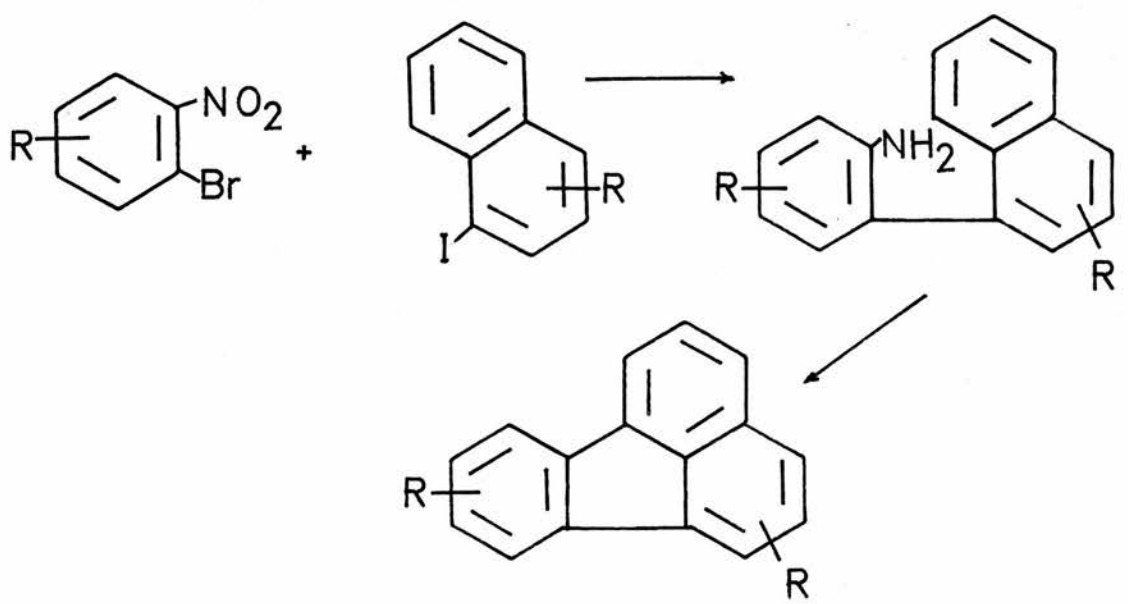
(57)

As mentioned (p.14), the 9-fluorenylsuccinic anhydride (25) can be cyclised to fluoranthene-1-carboxylic acid [53] which can be decarboxylated to fluoranthene.

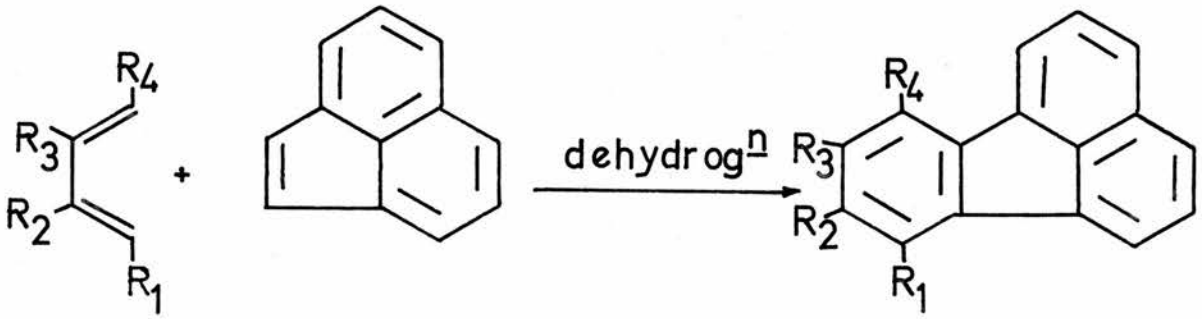


(25)

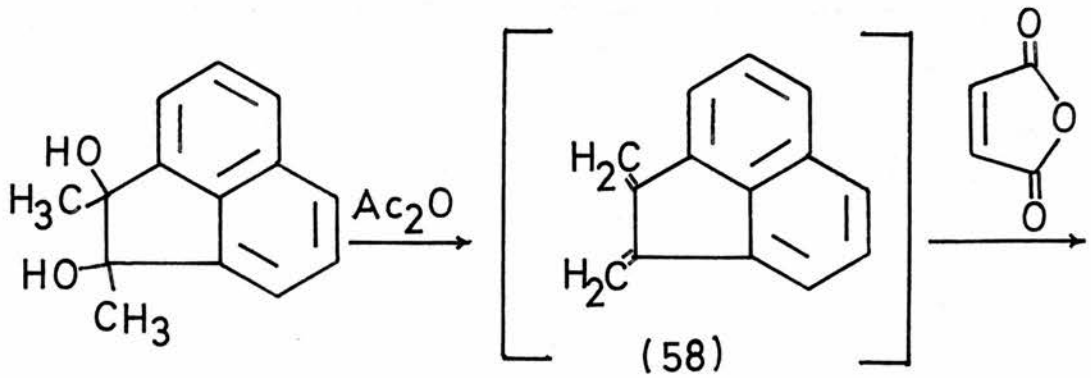
B. From naphthalene. Several substituted fluoranthenes have been synthesised by coupling 1-iodonaphthalenes with 2-bromonitrobenzenes by the Ullmann reaction [54]. The products were reduced to the corresponding amino-compounds, and the diazonium derivatives cyclised with copper-bronze.

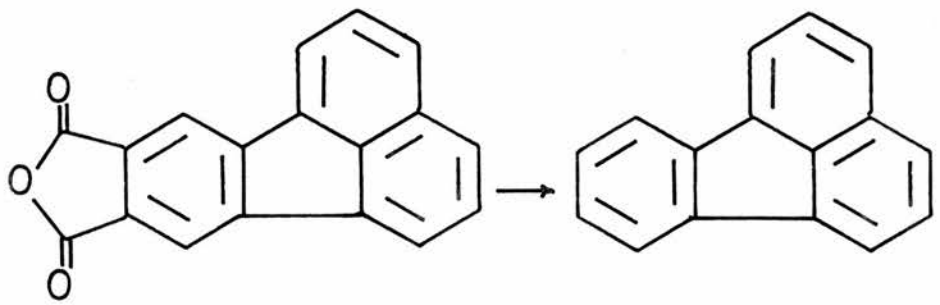


C. From the acenaphthene nucleus. Acenaphthylene undergoes Diels-Alder reaction with certain dienes to give substituted fluoranthenes [55,56,57].



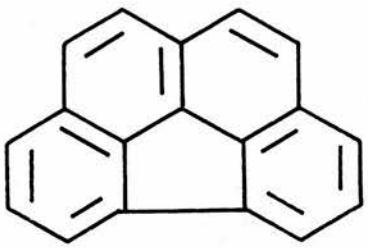
A Diels-Alder reaction with an acenaphthene derivative acting as an intermediate diene (58) and maleic anhydride gave [58] a fluoranthene anhydride which on decarboxylation and dehydrogenation gave fluoranthene.





Substitution. The substitution of fluoranthene is not involved in this present work. Suffice to mention that monosubstitution normally occurs in the 3-position, except with Friedel-Crafts reactions when the 8-position is the preferred point of attack. Disubstitution occurs in many other positions, principally the 9,8, and 2-positions.

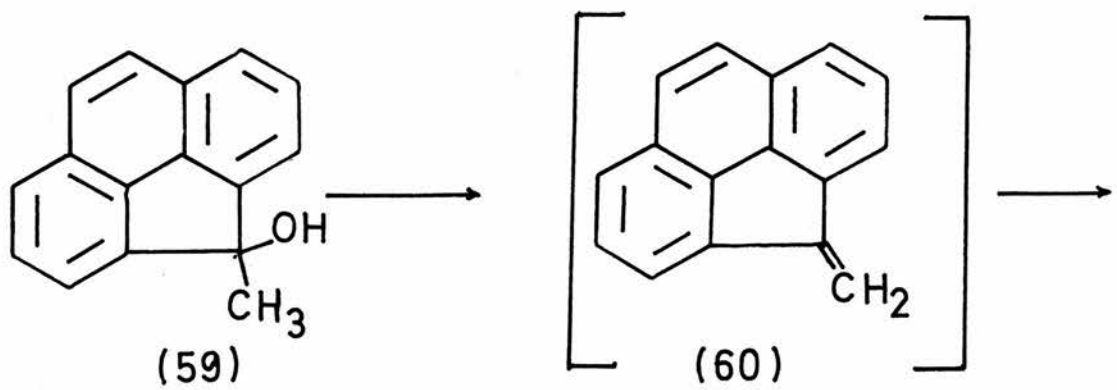
Benzo(ghi)fluoranthene.



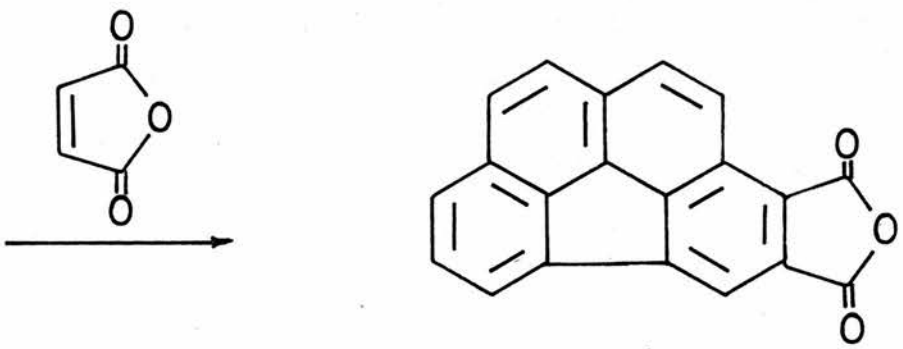
(4)

This hydrocarbon, the first known with four six-membered rings fused directly to a five-membered ring, was reported in 1952 having been synthesised by two routes [1].

The first synthesis was closely analogous to that of fluoranthene from 9-methylfluoren-9-ol and maleic anhydride (cf.p.25). A Diels-Alder type addition to the dehydration intermediate 60 from 4-methyl-4H-cyclopenta(def)phenanthrene-4-ol (59) with maleic anhydride gave benzo(ghi)fluoranthene-3:4-dicarboxylic acid anhydride (61), which decarboxylated to the hydrocarbon.

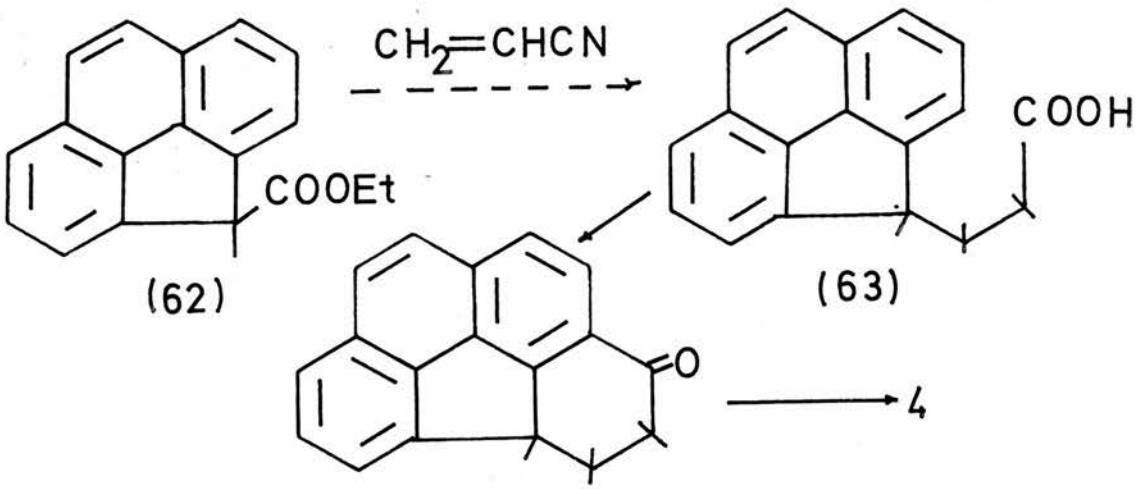


(59) (60)



(61)

The second synthesis of benzo(ghi)fluoranthene also parallels a synthesis of fluoranthene - that from β-9-fluorenylpropionic acid [59]. The Michael addition of ethyl 4H-cyclopenta(def)phenanthrene-4-carboxylate (62) and acrylonitrile was utilised to give, after hydrolysis and partial decarboxylation, 4H-cyclopenta(def)phenanthrene-4-β-propionic acid (63), which cyclised to 3:4:5:5a-tetrahydro-3-keto-benzo(ghi)fluoranthene (64). Reduction and dehydrogenation gave the hydrocarbon (4).



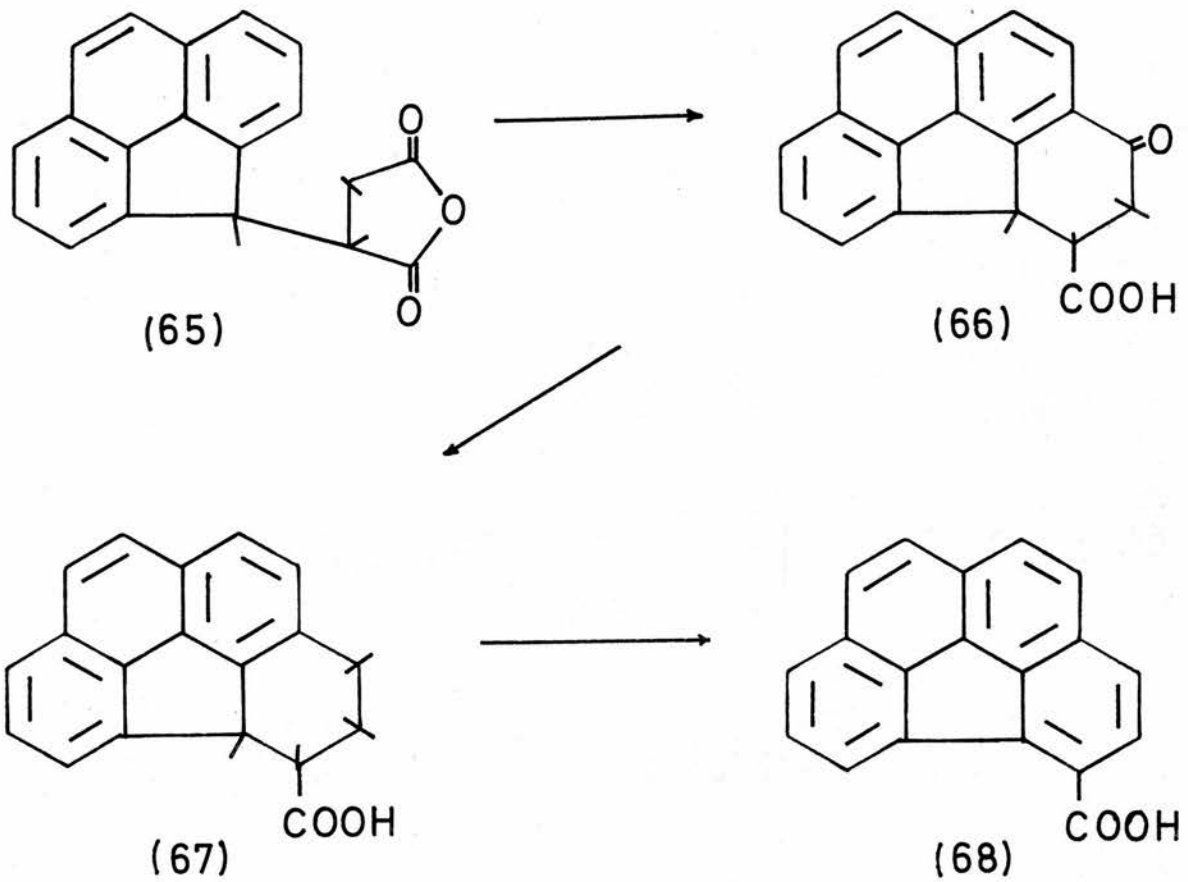
(62) (63) (64)

The hydrocarbon 4 has been isolated [60] from the coal-tar fraction boiling at 425°-428°C, and identified in tobacco-smoke condensate [61a], exhaust gases [61b], and in the many products of the high temperature pyrolysis of n-decane [62].

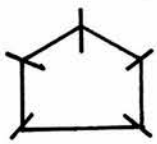
A detailed structural investigation by X-ray analysis has shown the molecule to be planar and symmetrical, with the strain inherent in such a structure distributed throughout the whole molecule [63]. The structure displays a marked tendancy towards having the maximum number of Kekule-type rings, as shown in the inset formula on page 28.

Benzo(ghi)fluoranthene-5-carboxylic acid (68) has been prepared [64]. Again paralleling a reaction known with fluorene (cf. p.14), 4H-cyclopenta(def)phenanthrene with maleic anhydride gave, as an intermediate, 4H-cyclopenta(def)phenanthrene-4-succinic anhydride (65), which cyclised with aluminium chloride as catalyst, to 3:4:5:5a-tetrahydro-3-keto-benzo(ghi)fluoranthene-5-carboxylic acid (66). Reduction to 3:4:5:5a-tetrahydro-benzo(ghi)fluoranthene-5-carboxylic acid (67), and dehydrogenation gave benzo(ghi)fluoranthen-5-carboxylic acid (68).

The present work has resulted in the synthesis of several other 5-substituted benzo(ghi)fluoranthenes.



Coronindene. The hydrocarbon coronindene (5) can be regarded as the ultimate member of the series of benzocyclopentanes embracing cyclopentane (69), hydrindene (70), acenaphthene (38), 4H-cyclopenta(def)phenanthrene (2), and benzo(ghi)fluoranthene (4).



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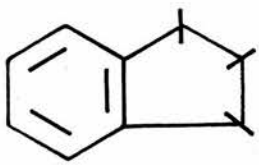

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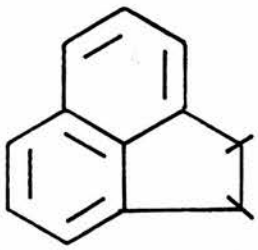

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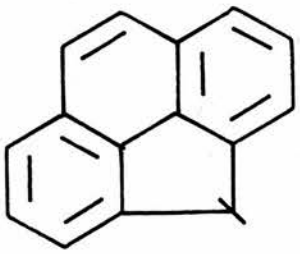

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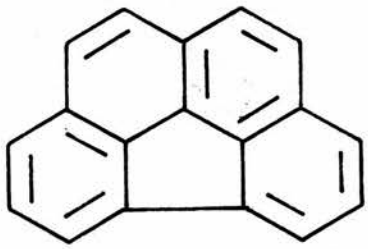


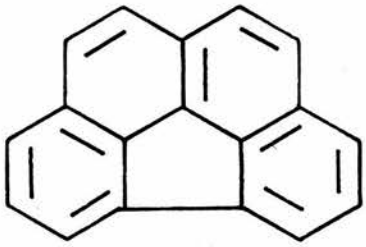
(4)

(5)

The hydrocarbon 5 has never been synthesised, and, indeed, doubts must be entertained as to whether such a structure can exist, in view of the great inherent strain implicit in such a polynuclear structure, demanding abnormal distortions of bond lengths and angles. Highly strained structures are, of course, known. A striking example is the recently synthesised cubane system [73].

Considerations of the Stereochemistry.

When considering the structure of coronindene, two analogous compounds come to mind, viz. benzo(ghi)fluoranthene (4) and coronene (71).



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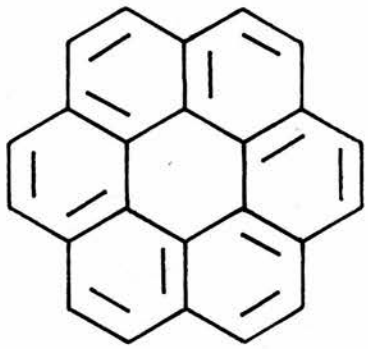


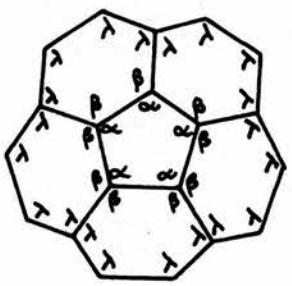
(71)

Benzo(ghi)fluoranthene because it is the member of the above series immediately preceding coronindene; and coronene, because it, like coronindene, is a polycyclic system consisting of a central ring completely surrounded by six-membered rings. The very obvious difference between the two coron-structures is that one has a central five—membered ring, the other a six-membered ring. This difference, as regards the strain in such structures, is all important. Strain is incurred when the demands of a particular structure force angles or bonds lengths to deviate from their values in completely strain-free structures - 120° and 1·39Å respectively in the case of aromatic systems.

The very essence of the symmetry of coronene demands no such deviations. A vastly different state of affairs exists, however, when the central ring is five-membered as

in coronindene. Two extreme stereochemical structures can be considered - planar and non-planar.

Planar structure. Coronindene is a symmetrical molecule, and thus it can be readily assumed that the strain will be equally distributed throughout the whole structure, in as much as corresponding bonds and angles will be equally affected. Thus it can be assumed that the central five-membered ring will be a regular pentagon with angles(α) of 108°.



The angles (β) of the six-membered rings at the positions of fusion to the five-membered ring are then 126°. An average angle (λ) of 117° can then be assigned to each of the four remaining angles of the six-membered rings. It is apparent that none of the angles can adopt the strainless value of 120° in this planar molecule, and thus some strain will exist in this stereochemical configuration.

Non-planar structure. In the planar structure the angles of the six-membered rings could not achieve the strain-free value of 120°. It is, however, possible for all the angles of the six-membered rings to be 120°, if the molecule is not planar, but "saucer-shaped", with the planes of the six-membered rings inclined at an angle to the plane of the five-membered ring.

Similar non-planar considerations of benzo(ghi)-fluoranthene [65] give exactly the same dimensions for each of the two structures, the additional six-membered ring of coronindene fitting exactly into the "vacant" position in the non-planar benzo(ghi)fluoranthene molecule. The calculations show that the angle the bonds common to two six-membered rings would make with the plane of the five-membered ring is 32°; the angle the planes of the six-membered rings would make with the plane of the five-membered ring is 37°; while the six-membered rings would be mutually inclined at 60° to each other.

Although the strain in the six-membered rings is eliminated in this non-planar structure, a strain factor, not present in the planar structure, is introduced, in as much as the internal carbon atoms, common to both five and six-membered rings cannot maintain sp^2-planarity.

Both the planar and non-planar conformations discussed above are equally applicable to coronindene and benzo(ghi)-fluoranthene. The latter compound has been shown to be

planar, which might indicate that this would also be the preferred conformation for coronindene. It must be borne in mind, however, that benzo(ghi)fluoranthene is not "tied" at the 5 and 6-positions, and, in its planar structure this "gap" is widened to minimise strain. In coronindene, this "gap" contains the fifth six-membered ring, which effectively ties the 5 and 6-positions together, thus not allowing for any lessening of strain as in the former compound. It may well be, therefore, that some conformation intermediate between the planar and non-planar structures discussed above would be that possessing the least structural strain energy for the completely symmetrical coronindene. The molecular geometry, and hence insight into how the strain is accommodated will best be determined by X-ray analysis. One of the advantages of this technique is that it only requires a very little material, albeit a fine crystalline specimen. As, if and when, coronindene is synthesised, it will be in very small amounts, perhaps in this field of molecular configuration interest will first lie.

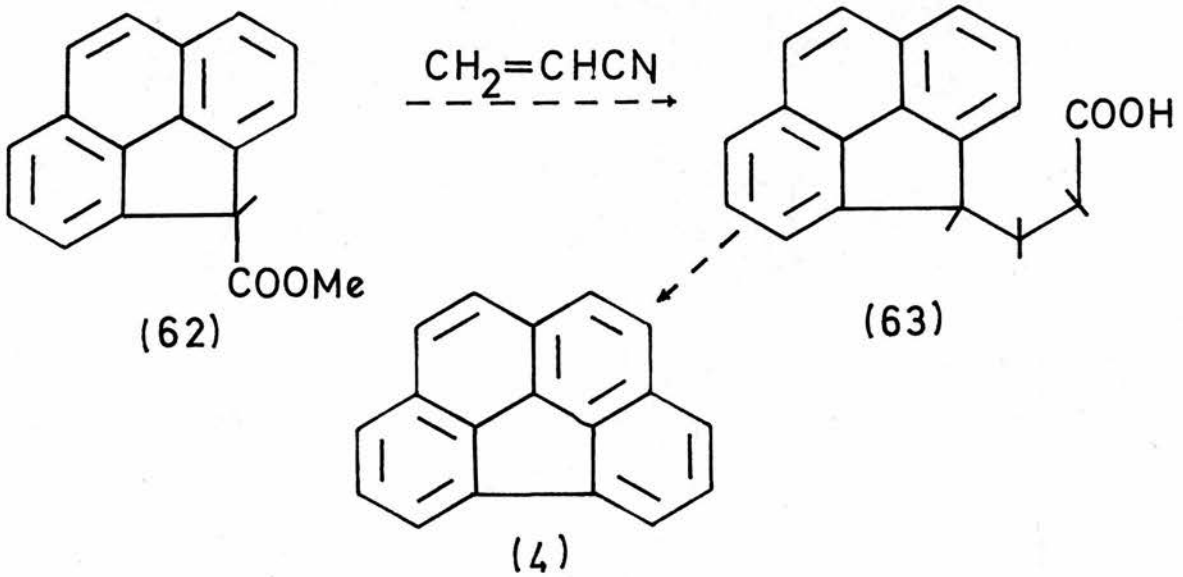
Object of the Research.

To synthesise Coronindene.

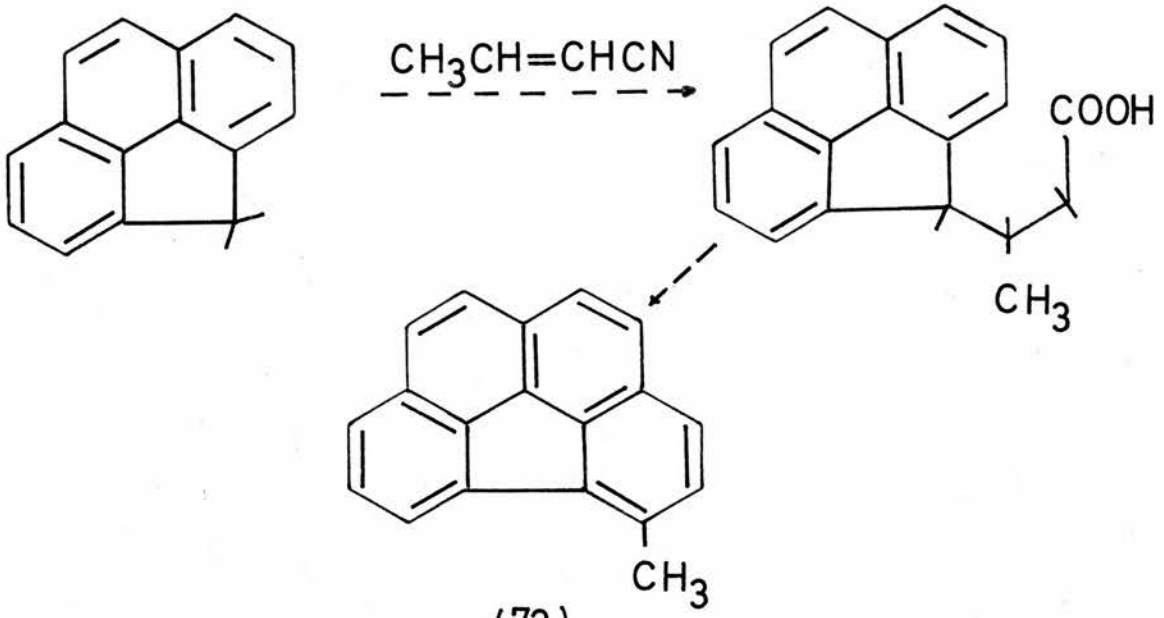
Introduction

Part II.

The basis of the synthesis employed towards coronindene was essentially an extension of the synthesis [1] of benzo(ghi)fluoranthene 4 (p.29). In this latter synthesis, one mole of acrylonitrile was condensed by a Michael addition reaction with ethyl 4H-cyclopenta(def)-phenanthrene-4-carboxylate (62) to give ultimately 4H-cyclopenta(def)phenanthrene-4-β-propionic acid (63) which was cyclised, reduced, and dehydrogenated to the desired hydrocarbon 4.

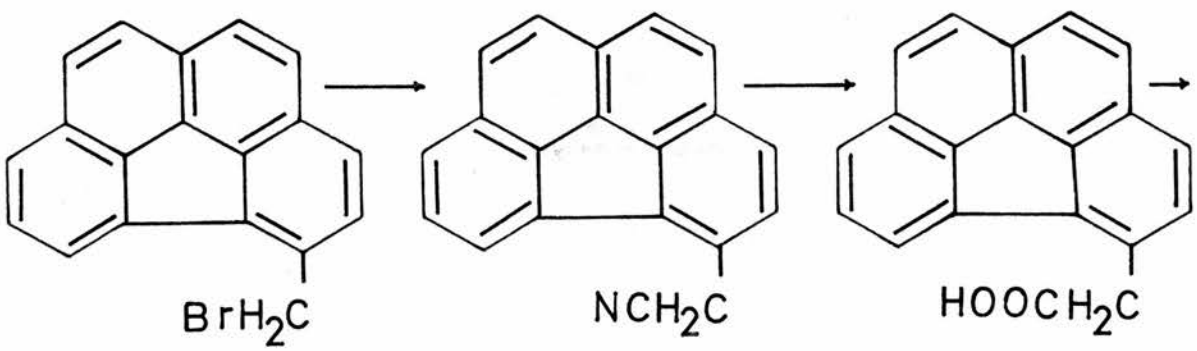


In the synthesis of coronindene, it was intended to employ crotonitrile in an analogous scheme to give 5-methylbenzo(ghi)fluoranthene (72).

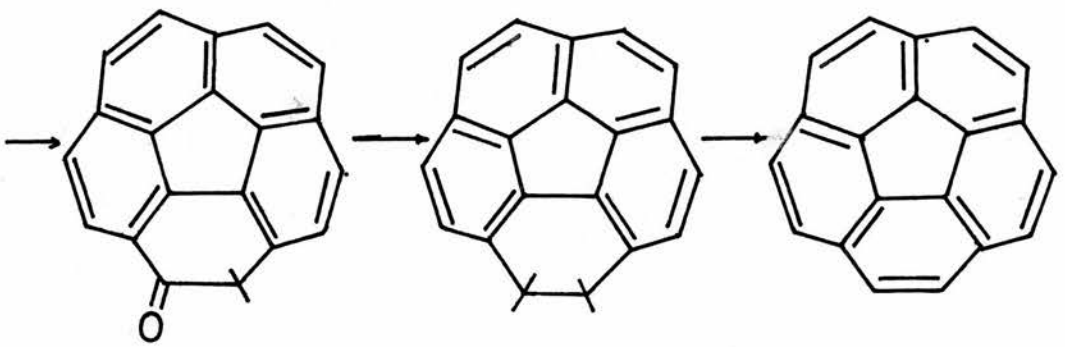


(72)

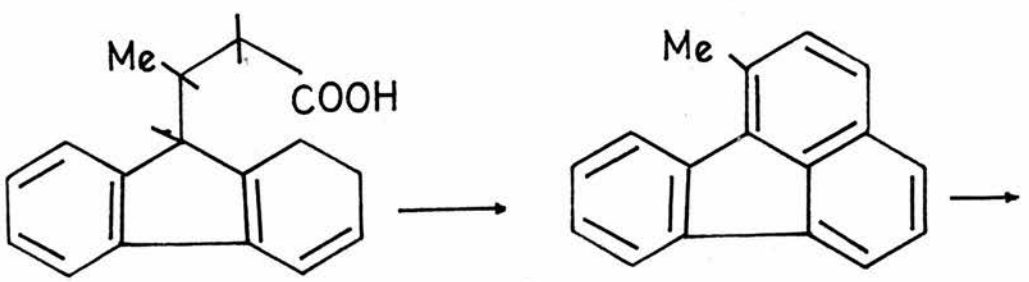
This methyl group provides a centre on which the final ring of coronindene may be built. The subsequent steps visualised side-chain bromination, followed by cyanation and hydrolysis to the acid 73, which on cyclisation, reduction and dehydrogenation, would afford coronindene.



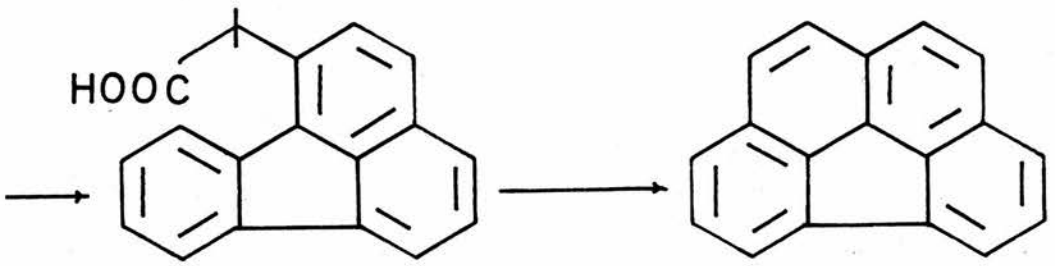
(73)



4H-cyclopenta(def)phenanthrene is a very expensive chemical, and not one with which to embark on such a proposed synthesis without first having "gone over the ground". To this end a trial synthesis anticipating the proposed synthesis as closely as possible was desirable. Fluorene, as a rather common cousin, but with the family reactions, presented itself as an admirable guinea-pig in this respect. It will be seen that applying the synthetic scheme outlined above to fluorene, 1-methylfluoranthene (56), formed by the first cyclisation [37], on bromination, cyanation, etc., gives benzo(ghi)fluoranthene.



(56)

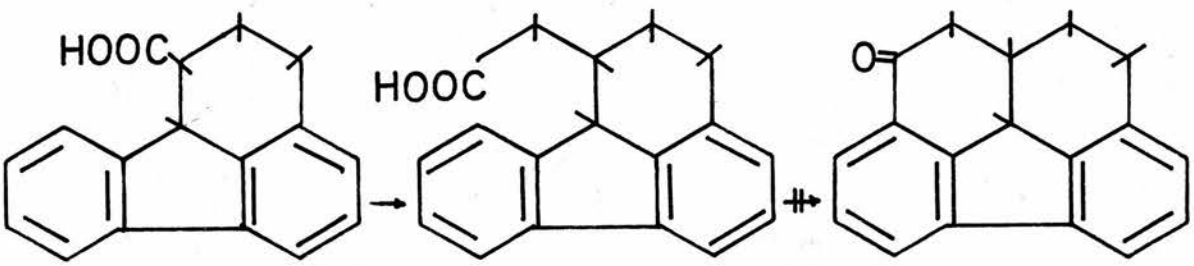


This forerunner to the coronindene synthesis is thus a very happy experiment, as, not only does it pave the way for greater things to come, but it also offers a new synthetic route to benzo(ghi)fluoranthene. It has the further merit that the final product is known, and thus the successful outcome of the synthesis can be readily established.

In brief, fluoranthene can be synthesised by adding one ring from the methylene position of fluorene, and benzo(ghi)fluoranthene by adding one ring from the methylene position of 4H-cyclopenta(def)phenanthrene. Can benzo(ghi)fluoranthene be prepared by adding two rings from the methylene position of fluorene; and coronindene likewise from 4H-cyclopenta(def)phenanthrene?

Some attempts have been made to synthesise benzo(ghi)-fluoranthene and some of its derivatives starting from fluorene, but mostly without success [66,67].

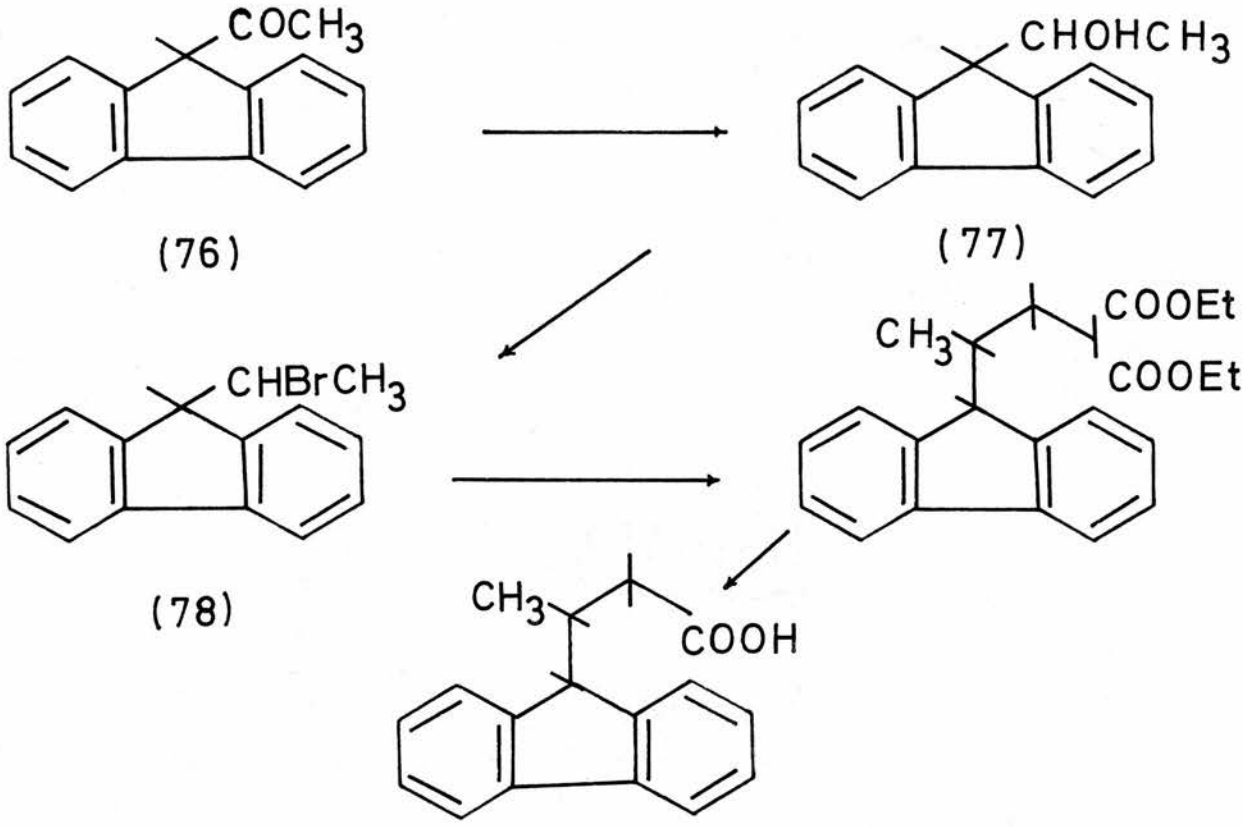
The reaction mentioned in the introduction (part I p.30) between fluorene and maleic anhydride, gives, on cyclisation and reduction, 1-carboxy-1:2:3:10b-tetrahydrofluoranthene (74). Swan [66] used the Arndt-Eistert reaction to give 1:2:3:10b-tetrahydrofluoranthene-1-acetic acid (75), which could not be cyclised.



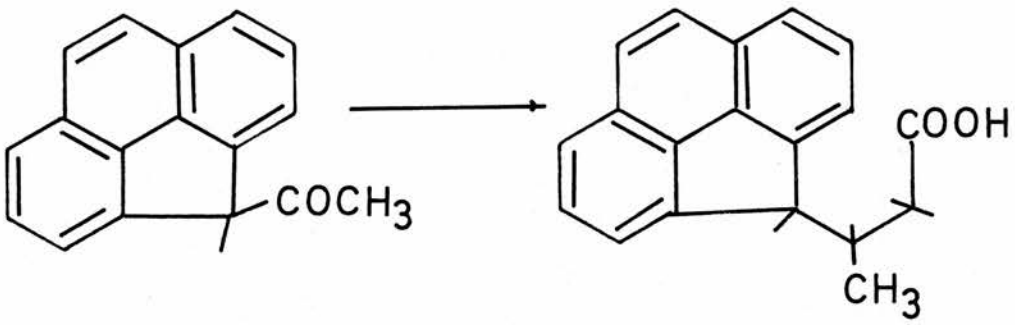
(74) (75)

This same worker attempted schemes of a similar nature to those proposed above. 1-methylfluoranthene (56) has been prepared by the cyclisation of the hydrolysed Michael addition product of fluorene and crotononitrile. As indicated, it is the intention of the present work to apply this reaction analogously with 4H-cyclopenta(def)phenanthrene in the hope of obtaining 5-methylbenzo(ghi)fluoranthene. Swan prepared 1-methylfluoranthene by the reduction of 9-acetylfluorene (76) (cf.p.14) to the corresponding carbinol [77], conversion of this into the bromide 78 and condensation with sodio-malonic ester gave, on hydrolysis, and decarboxylation

the same butyric acid intermediate 79 as is obtained using crotononitrile. This, of course, had been cyclised to 1-methylfluoranthene.



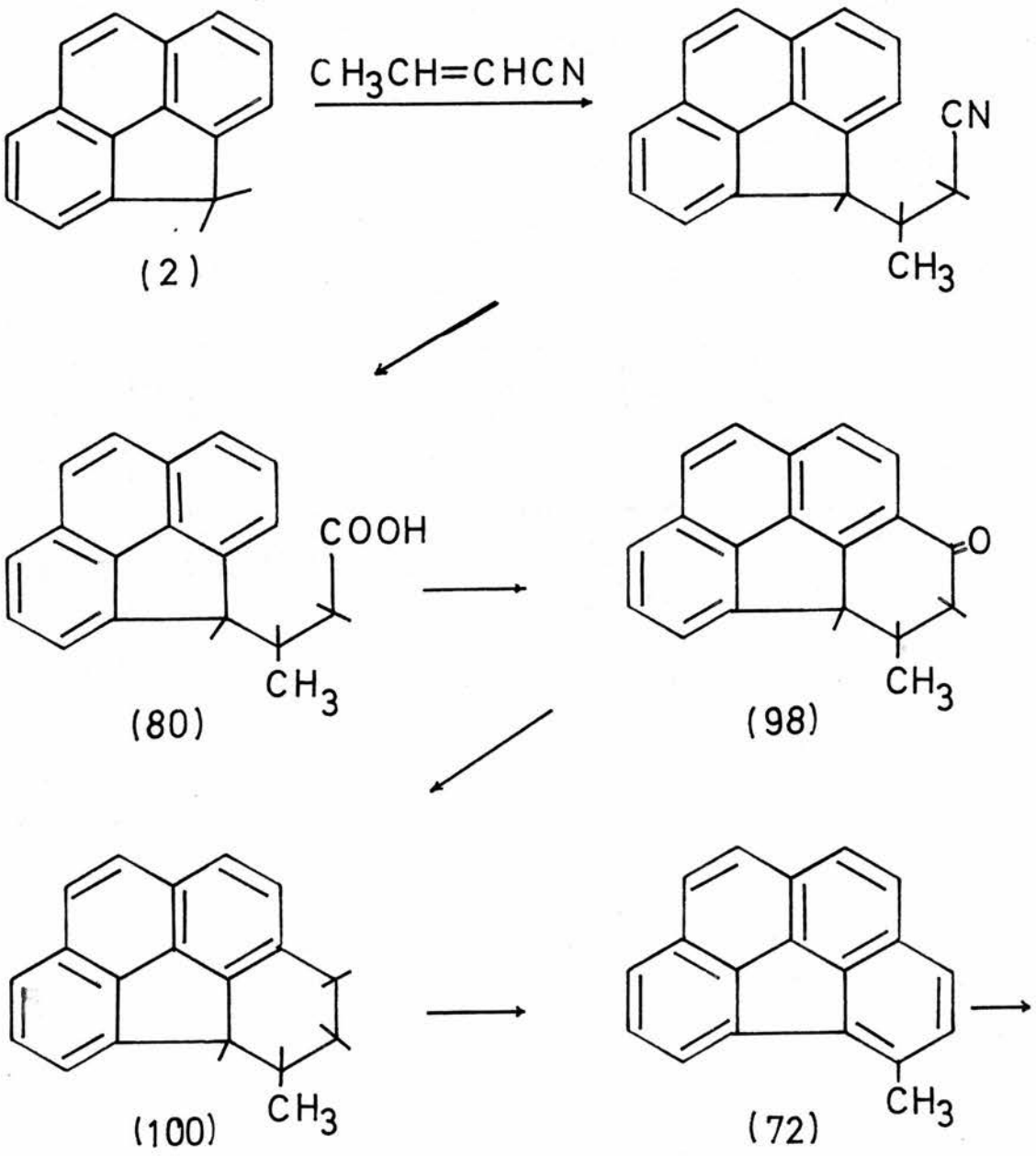
Extension of this method to 4H-cyclopenta(def)phenanthrene proceeded less satisfactorily to β-4H-cyclopenta(def)phenanthrenyl-butyric acid (80), subsequent cyclisation not being attempted due to lack of material.

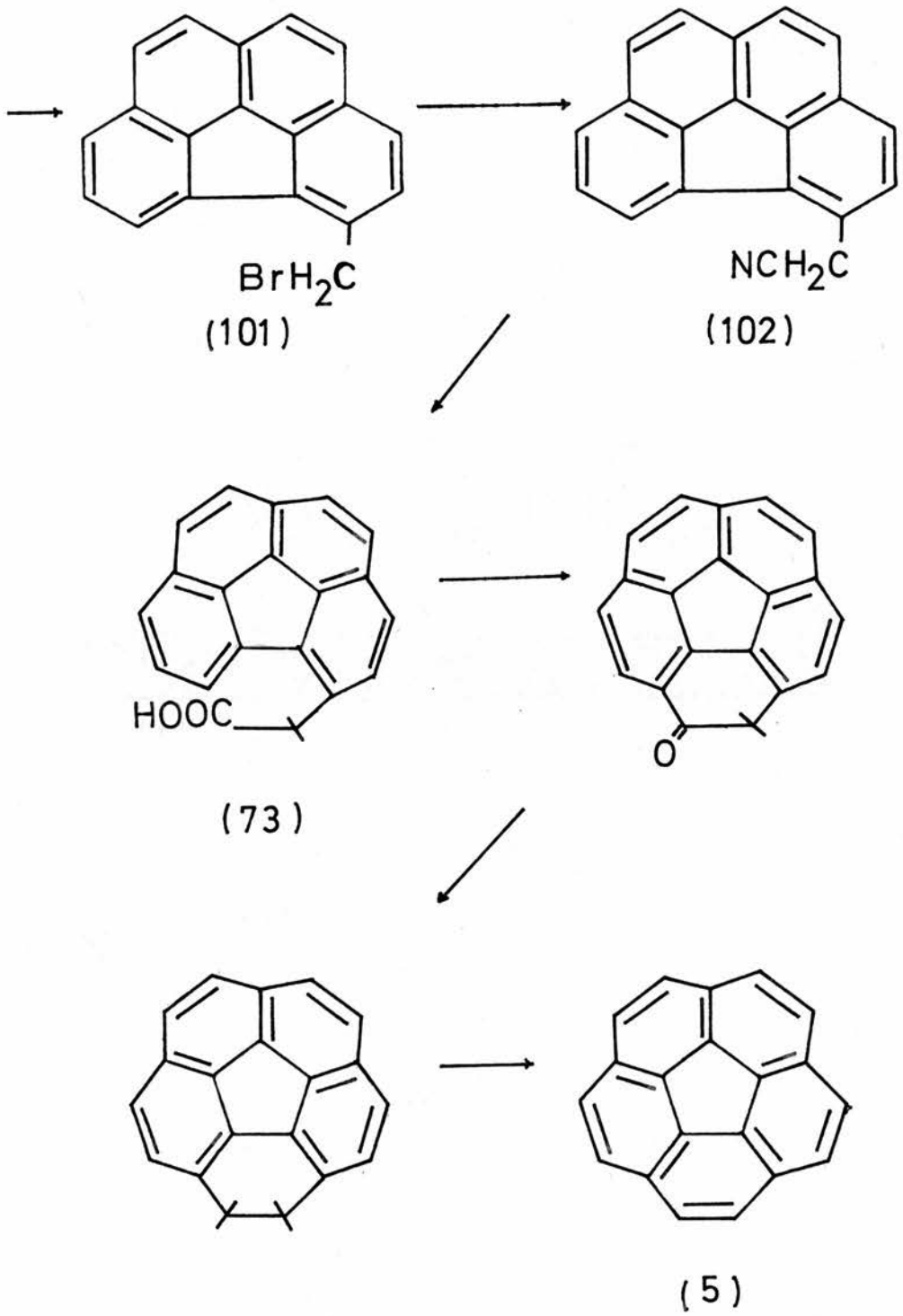


(80)

Discussion of Results.

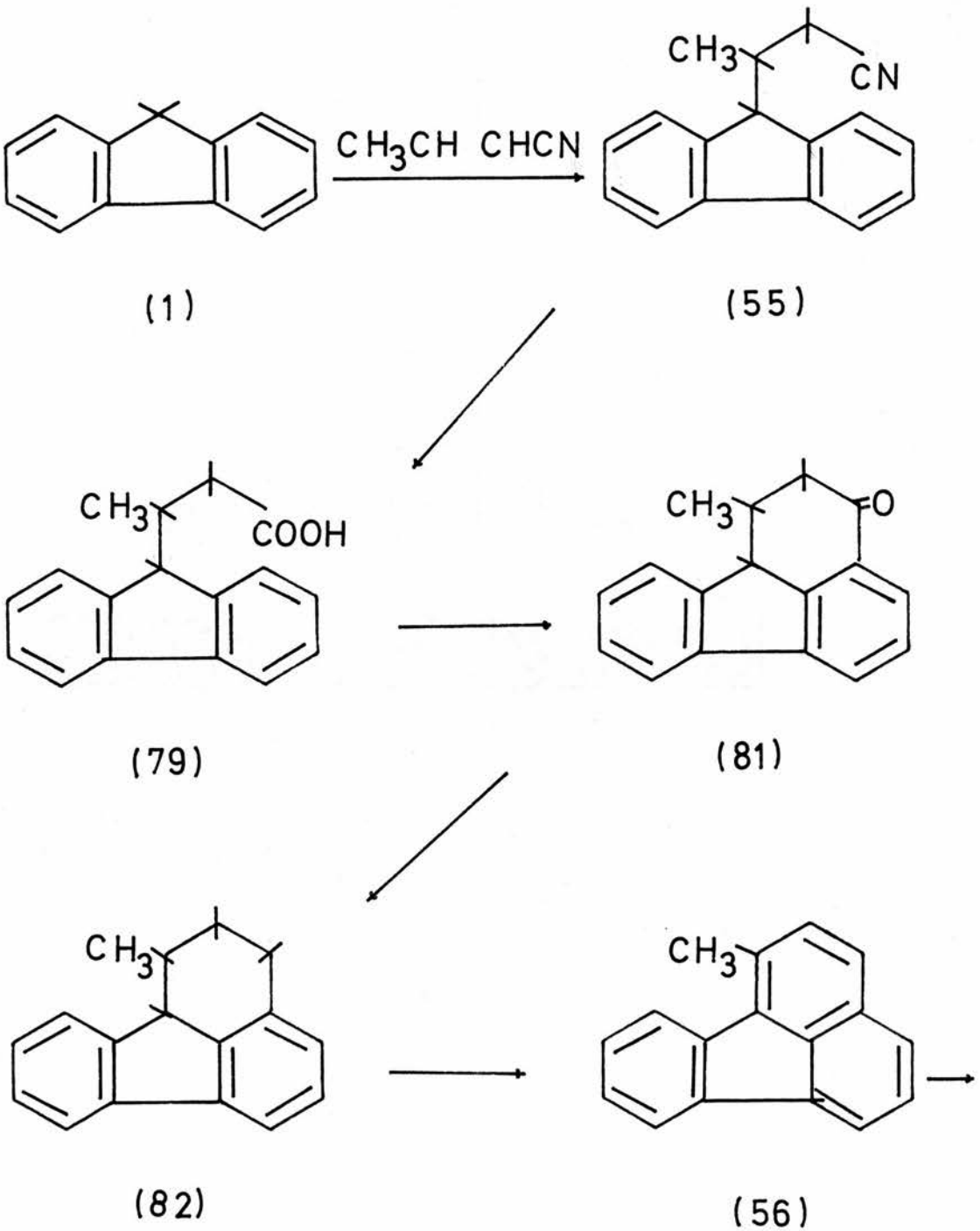
The scheme intended for the synthesis of coronindene is given in detail below:-

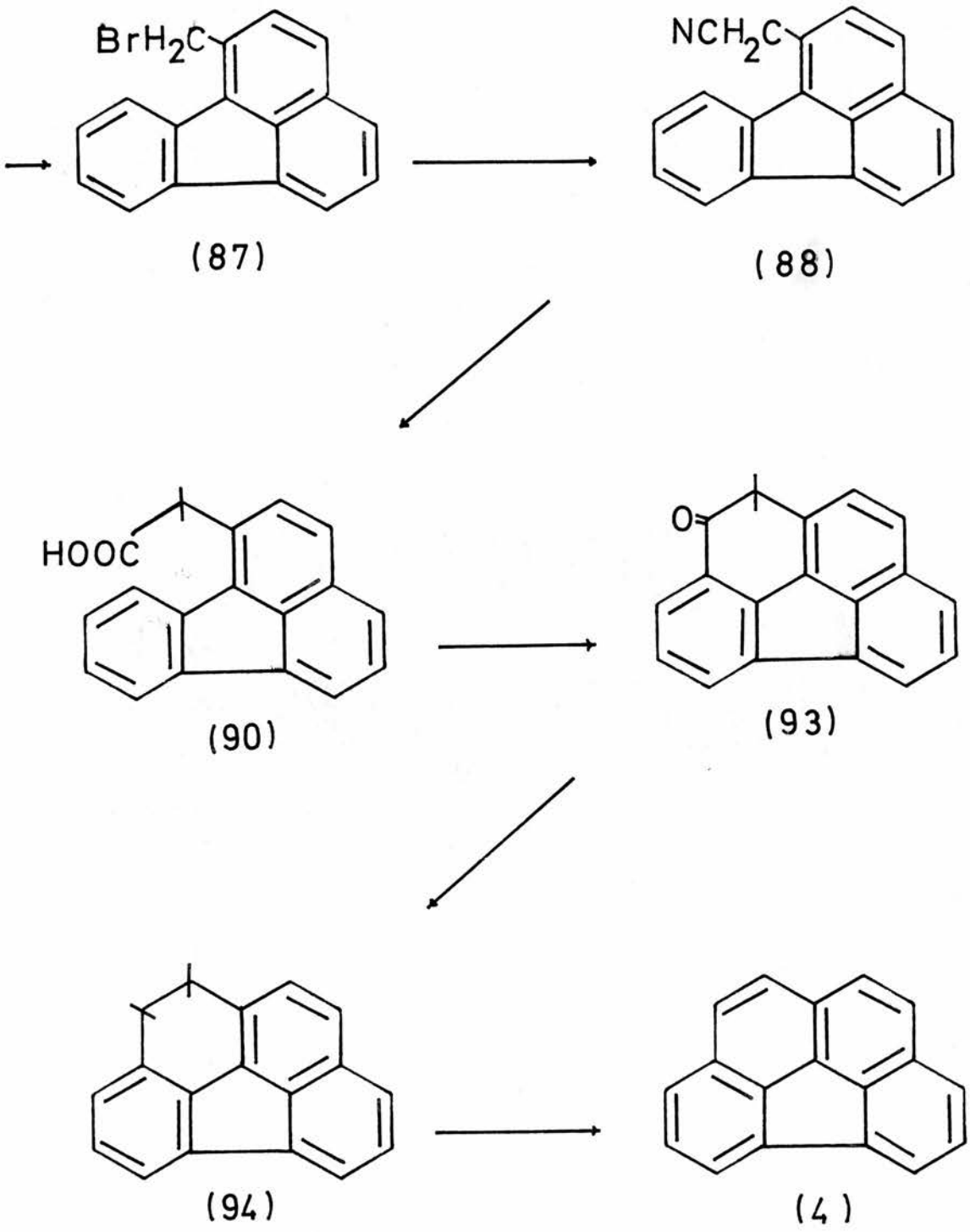




(101) (102) (73) (5)

The corresponding synthesis related to fluorene is, therefore:-





(87) (88) (90) (93) (94) (4)

As indicated in the introduction, this latter synthesis was undertaken first.

1-Methylfluoranthene (56) has previously been synthesised [37] by a route very closely analogous to the one employed in this work. Brunson [34] showed that in the presence of base, although two molecules of acrylonitrile add to one molecule of fluorene, only one molecule of crotononitrile adds analogously. It was also shown that the isomeric allyl cyanide and crotononitrile react to give the same product, the allyl cyanide undergoing isomerisation to the more stable crotononitrile prior to reacting.

$$CH_2=CHCH_2CN \overset{B^{\ominus}}{\rightleftharpoons} CH_3CH=CHCN$$

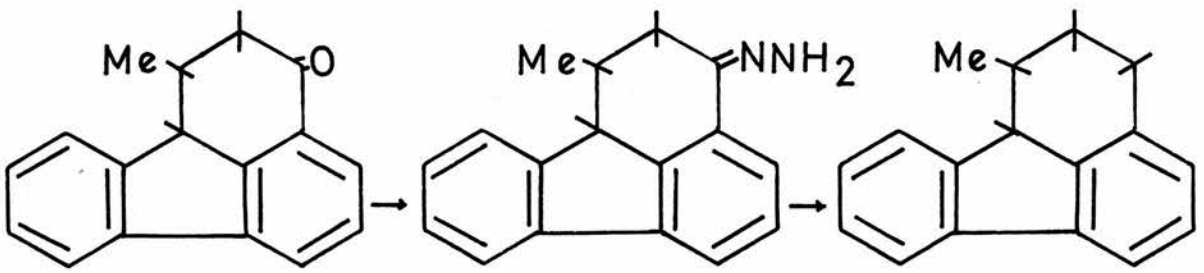
Tucker [37] condensed allyl cyanide with methyl fluorene-9-carboxylate, which served to activate the 9-position still more. Hydrolysis and decarboxylation removed the 9-carbomethoxy group to give β-9-fluorenylbutyric acid (79). In the present work, a combination of these two syntheses was employed.

β-9-fluorenyl propyl cyanide (55) was prepared direct from fluorene by the method of Brunson [34], hydrolysis to β-9-fluorenylbutyric acid (79) being achieved by boiling with potassium hydroxide in 2-methoxyethanol as described by Tucker [37]. This latter worker subsequently cyclised β-9-fluorenylbutyric acid (79) to 1-methyl-3-keto-1:2:3:10b-tetrahydrofluoranthene (81) by the action of stannic chloride on the acid chloride prepared by the action of thionyl chloride on 79.

This work was repeated, but it was found that the product was always discoloured, orange needles with the same melting-point as Tucker's cream-coloured leaflets being obtained.

Cyclisation, therefore, was carried out with anhydrous hydrogen fluoride. This modification was found to be much superior, giving a purer product in increased yield. Reduction of the cyclic ketone 81 to 1-methyl-1:2:3:10b-tetrahydro-fluoranthene (82) was carried out by Tucker using the Huang-Minlon modification of the Wolff-Kishner reduction, in which the hydrazone is made insitu.

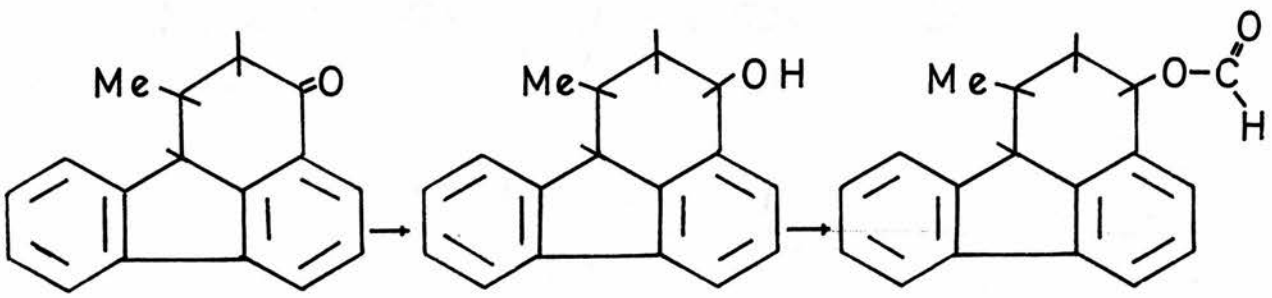
Repetition of this work gave a yield of 42% as compared with the reported 46%, both of which constitute a drastic loss in material. Various modifications were considered, the most satisfactory being that in which the hydrazone 83 was isolated and purified before being treated with alkali, i.e., a Wolff-Kishner reduction in two stages.



(81) (83) (82)

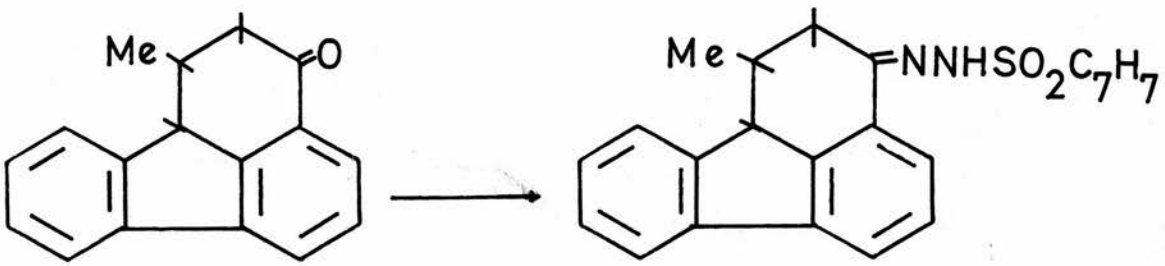
A further improvement to the method used by Tucker was not to filter and crystallise the precipitate obtained on acidification of the alkaline mixture with hydrochloric acid, but to extract and chromatograph through alumina. These modifications resulted in a purer product in a much improved overall yield of 75%.

Two methods of reduction were investigated. In the first, the ketone 81 was reduced with sodium borohydride to the corresponding carbinol, 1-methyl-3-hydroxy-1:2:3:10b-tetrahydrofluoranthene (84), dehydration and dehydrogenation of which would afford 1-methylfluoranthene. Attempted dehydration with formic acid resulted in formation of the formyl ester 85.



(81) (84) (85)

The second method was by the sodium borohydride reduction of the toluene-sulphonyl hydrazone [68]. 1-methyl-3-keto-1:2:3:10b-tetrahydrofluoranthene-tosylhydrazone (86), (m.p. 240°C.), was prepared from the ketone 81 by reaction with tosylhydrazide.

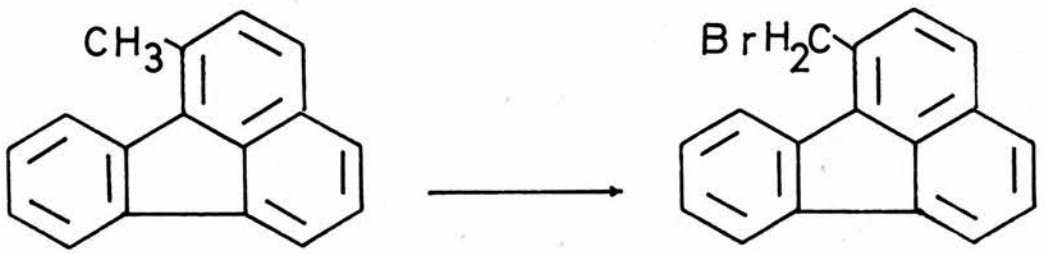


(81) (86)

Attempts at reduction were unsuccessful, unchanged starting material being obtained with methanol as solvent, and a very little amorphous yellow compound, (m.p. 260°C.), with dioxan as solvent.

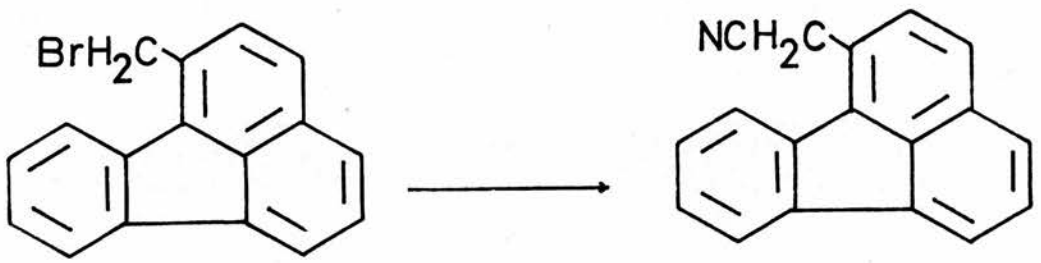
The tetrahydro derivative 82 was readily dehydrogenated with chloranil by the method of Tucker. It was again found advantageous to chromatograph the crude reaction product through alumina before attempting crystallisation.

The methyl group of 1-methylfluoranthene (56) was readily brominated to 1-bromomethylfluoranthene (87) by boiling with N-bromosuccinimide and peroxide catalyst.



(56) (87)

The next stage in the synthesis involved cyanation of 1-bromomethylfluoranthene (87) to fluoranthene-1-acetonitrile (88).



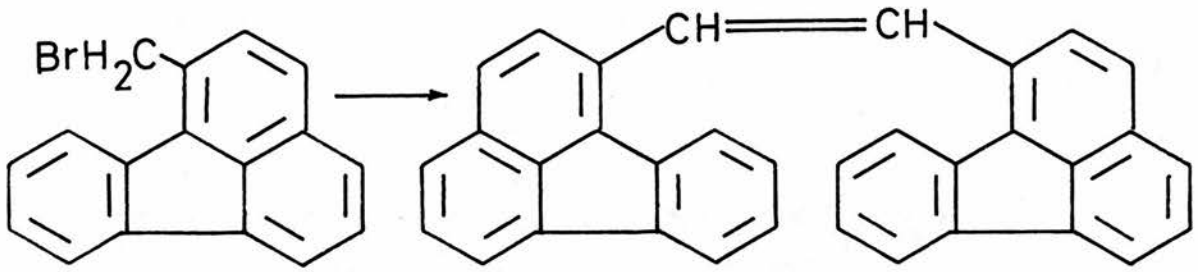
(87) (88)

This stage in the synthesis proved the most troublesome. It was found very difficult to convert this bromo-compound to the corresponding nitrile with metal cyanides. Such nucleophilic reactions are known to take place very much more quickly in aprotic solvents [69].

On warming 1-bromomethylfluoranthene and sodium cyanide in anhydrous dimethylsulphoxide (DMSO), the

solution became dark red, solid beginning to separate after a few minutes. This solid, which contained no nitrogen or halogen, and analysed for a hydrocarbon, is most probably the dimer 1:2-di-1-fluoranthenyl-ethylene (89), formed as indicated.

$$RCH_2Br \xrightarrow{-H^+} \bar{R}CHBr \xrightarrow{RCH_2Br} RCHBr-CH_2R \xrightarrow{-HBr} RCH=CHR$$

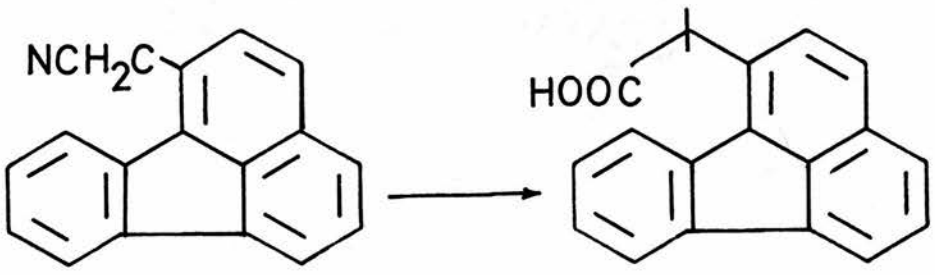


(87) (89)

Fluoranthene-1-acetonitrile (88) was obtained from this reaction primarily as a crude solid, purification of which resulted in a drastic loss of material. Although a yield of 61% of crude nitrile was obtained on one occasion by this method, yields were mostly very much lower, crude tarry material and the dimer accounting for most of the starting material. Ethanol was tried as a solvent, but the bromide was found to be too insoluble. When the reaction was attempted in boiling AnalaR acetone with sodium cyanide and potassium iodide [70], the only product isolated was the dimer 89. The use of the

aprotic solvents dimethylformamide and N-methylpyrolidone gave tarry products. 2-methoxyethanol as solvent gave reasonable yields of crude nitrile together with tarry material.

This stage may be summed up as most unsatisfactory, low yields of crude nitrile being the result of most attempted cyanations. However, by dint of sacrifice of much 1-bromomethylfluoranthene, crude fluoranthene-1-acetonitrile could be obtained. Hydrolysis of this nitrile 88 to the corresponding fluoranthene-1-acetic acid (90) was achieved by the method previously employed - boiling with potassium hydroxide in aqueous 2-methoxy-ethanol.

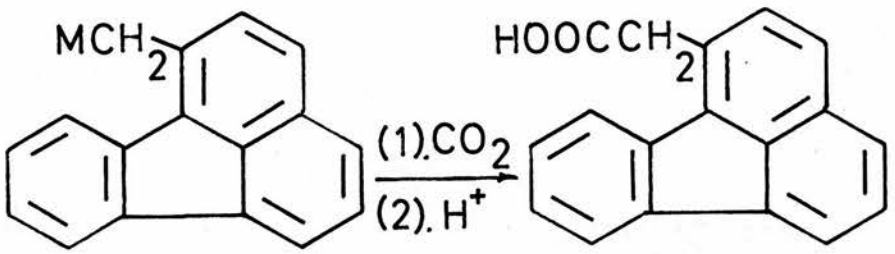


(88) (90)

This gave a deep purple colour immediately on adding the alkali. This mixture, having been boiled until ammonia ceased to be evolved, was diluted with water and extracted with ether to remove the red colour. Acidification of the aqueous layer precipitated the acid,

which it was found better to extract rather than filter. Being very insoluble in benzene, fluoranthene-1-acetic acid was crysrallised from decalin.

Attempts were made to synthesise fluoranthene-1-acetic acid directly from 1-bromomethylfluoranthene by carbonation of the corresponding organo-metallic reagent 91 (M=Na or Li).



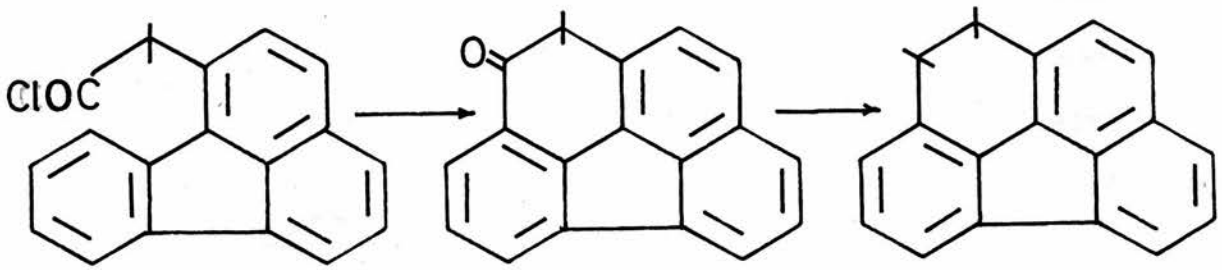
(91) (90)

However, no reaction could be induced with 1-bromomethyl-fluoranthene (91 M=Br) and either magnesium or lithium.

After its conspicuous success in the synthesis of the first ring, the cyclisation of fluoranthene-1-acetic acid to 2-keto-1:2-dihydrobenzo(ghi)fluoranthene (93) was attempted with anhydrous hydrogen fluoride. Unfortunately, fluoranthene-1-acetic acid was insoluble in hydrogen fluoride, as was the acid chloride (92), prepared by the action of thionyl chloride. Cyclisation of the acid chloride was next attempted with stannic chloride, but, after work-up, most of the starting material was accounted for as regenerated acid.

Cyclisation of the acid chloride was achieved with

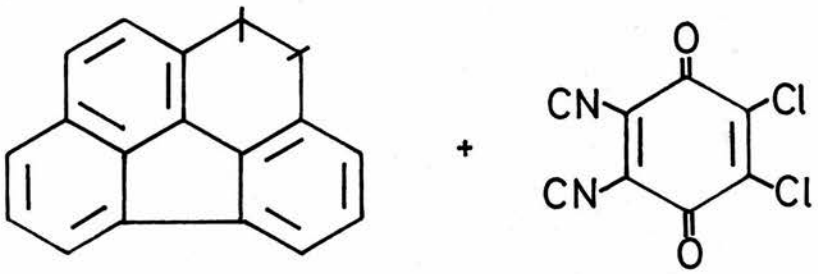
aluminium chloride in methylene chloride.



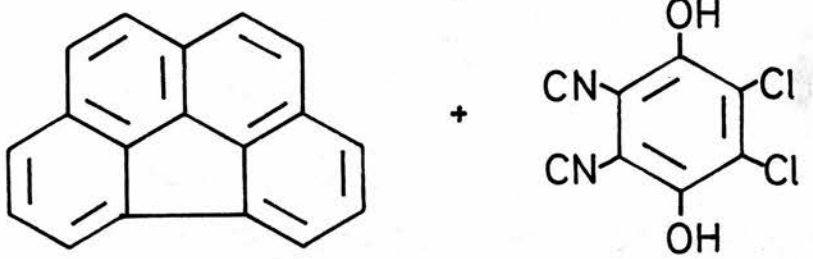
(92) (93) (94)

The cyclic ketone 93 was obtained as a pale yellow, amorphous, highly insoluble solid. Conversion to 1:2-dihydrobenzo(ghi)fluoranthene (94) was carried out by a modification of the Huang-Minlon[116] Wolff-Kishner reduction. The ketone (93) was allowed to react in diethylene glycol with hydrazine hydrate before addition of potassium hydroxide, in an attempt to ensure formation of the intermediate hydrazone.

The final stage in this synthesis was dehydrogenation to benzo(ghi)fluoranthene, achieved by boiling the dihydro-derivative with 2:3-dichloro-5:6-dicyanobenzoquinone in sulphur-free xylene. The reaction proceeded smoothly, an almost quantitative yield of the diphenol 95 separating out.



(94)



(4)

(95)

Chromatography of the product through alumina gave fine pale, yellow needles. Unfortunately, very little of this material was obtained, and the crystals were rather oily. In consequence, no satisfactory melting-point was obtained. However, on adding a saturated solution of picric acid in benzene to a benzene solution of these crystals and contaminant oil, an orange precipitate immediately separated. This material crystallised from ethanol saturated with picric acid as fine orange needles, the melting-point of which agreed with that of the dipicrate of benzo(ghi)fluoranthene [1].

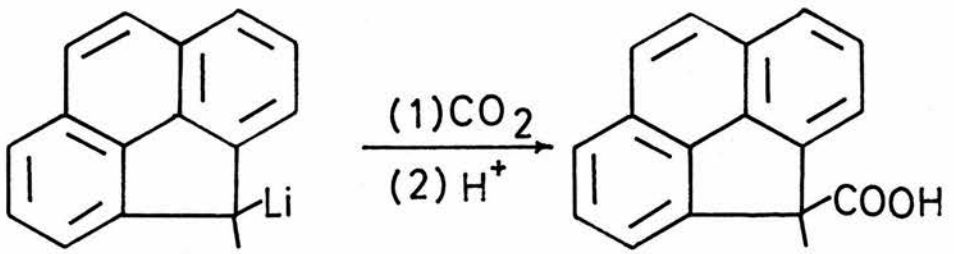
Summary of this synthesis. As a preliminary investigation of the synthetic procedures to be used in the synthesis of coronindene, what has the above synthesis indicated? It is possible to add two rings around the methylene position of fluorene, but it will naturally be harder to cyclise the final ring of coronindene, due to the greater rigidity of the four-ringed skeleton. The indications are that the most troublesome stage will be the cyanation of the corresponding bromomethyl compound.

Attempted synthesis of Coronindene.

In the synthesis of benzo(ghi)fluoranthene from 4H-cyclopenta(def)phenanthrene and acrylonitrile [1] it was necessary to employ the 4-carbomethoxy derivative 62, not so much to activate the remaining 4-hydrogen atom, as to block this 4-position to the addition of two molecules of acrylonitrile. For similar reasons ethyl fluorene-9-carboxylate was employed in the synthesis of fluoranthene [59]. However, only one molecule of crotononitrile adds to fluorene, thus obviating the use of the ester. A parallel was anticipated in the reaction between 4H-cyclopenta(def)phenanthrene and crotononitrile. This condensation, however, could not be achieved with a variety of basic catalysts and solvents, unchanged starting materials being recovered. This failure to react perhaps reflects a lesser activity of the methylene position of 4H-cyclopenta-(def)phenanthrene as compared to fluorene (cf. p.22).

It was necessary to employ the 4H-cyclopenta(def)-phenanthrene-4-carboxylic ester in this initial stage, which was unfortunate, as the introduction of an extra step when using the vastly more expensive of the methylene compounds was not desirable. Mention is made in the Introduction (p.23) of methyl 4H-cyclopenta(def)phenanthrene-4-glyoxalate (51), the hydrogen peroxide oxidation of which was employed [1] in the preparation of 4H-cyclopenta(def)phenanthrene-4-carboxylic acid (96). Apart from requiring a week to reach completion, this method was found to be unreliable, 4-keto-4H-cyclopenta-(def)phenanthrene (33) being the major product on several occassions. A superior method was the carbonation and

acidification of the organo-metallic compound 4-lithio-4H-cyclopenta(def)phenanthrene (97) formed by the exchange of lithium between 4H-cyclopenta(def)phenanthrene and phenyllithium.



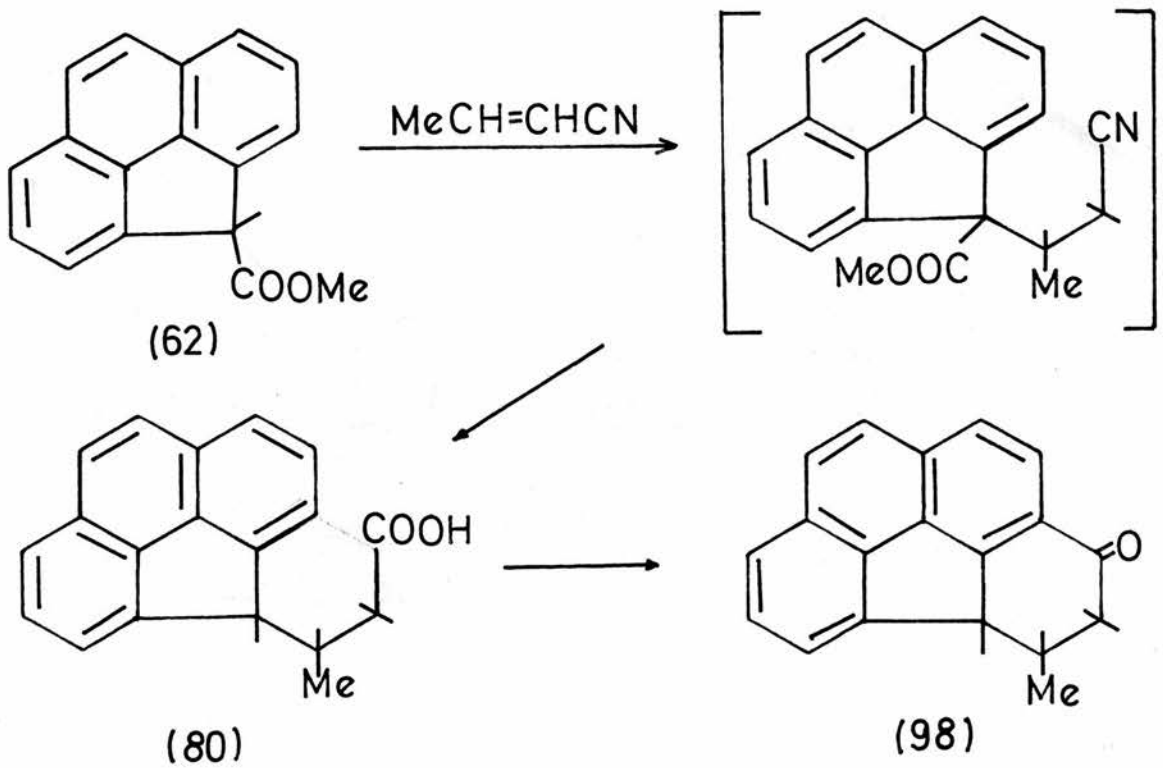
(97) (96)

It was found essential to use the "batch" process of carbonating described in the experimental section. Otherwise, adding the ethereal solution of 97 dropwise on to a stirred mass of finely crushed solid carbon dioxide resulted in greatly reduced yields of 96.

Methyl 4H-cyclopenta(def)phenanthrene-4-carboxylate (62) was formed in quantitative yield from the acid with diazomethane.

A control experiment showed that crotononitrile added to 62 much more slowly than did acrylonitrile. The desired addition of 62 with crotononitrile was achieved by maintaining the reactants at 40-45°C. in 2-methoxyethanol for 4-5 days with potassium hydroxide as catalyst. This contrasts with the

reaction time of one hour at room-temperature with acrylonitrile. No attempt to isolate the intermediate nitrile was made, and boiling with additional solvent and potassium hydroxide effected hydrolysis and partial decarboxylation to β-4H-cyclopenta(def)phenanthrenylbutyric acid (80).

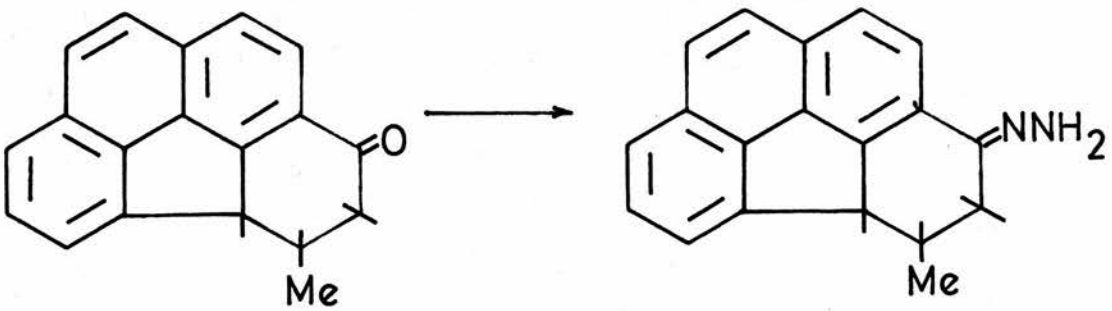


(62) (80) (98)

As mentioned in the Introuction (p.42), this acid had previously been obtained impure, the melting-point of the present sample showing an elevation of ca. 13-15°C. over that reported. Fears that this acid, 80, like the previous isomeric four-ringed acid, 90, might not be soluble in hydrogen fluoride proved unfounded, cyclisation to 5-methyl-3-keto-3:4:5:5a-tetrahydrobenzo(ghi)fluoranthene (98) being achieved in good yield by this very clean method - 76% compared with 52% with stannic chloride on the unsubstituted

structure [1].

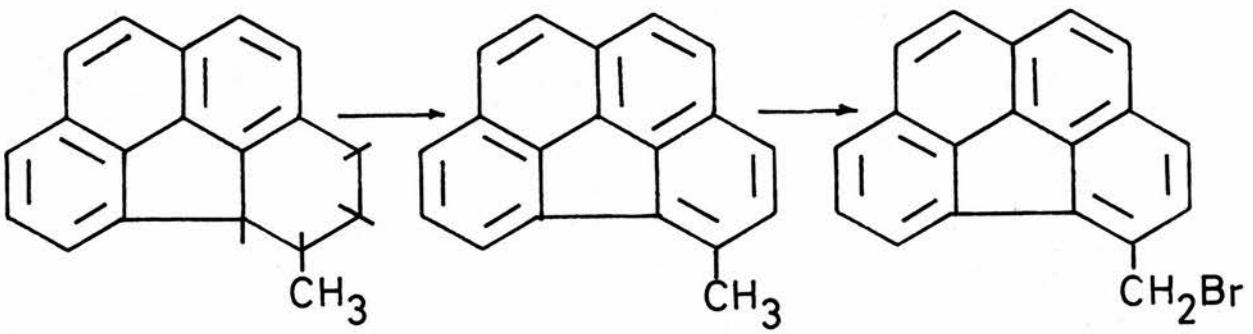
As before, reduction of the cyclic ketone was carried out in two stages, the hydrazone 99 being isolated and purified, rather than merely formed in situ. Although not very soluble in ethanol, a suspension of the ketone 98, when boiled in ethanol with hydrazine hydrate, gave an almost quantitative yield of the hydrazone. The ketone gradually dissolved as it reacted, thus obviating the need for large amounts of solvent, which had only to be subsequently removed in order to obtain the very much more soluble 5-methyl-3-keto-3:4:5:5a-tetrahydrobenzo(ghi)fluoranthene hydrazone (99).



(98) (99)

Decomposition of the hydrazone to the hydrocarbon proceeded smoothly, 5-methyl-3:4:5:5a-tetrahydrobenzo(ghi)-fluoranthene (100) crystallising from ethanol as pale, yellow needles after purification by chromatography on alumina.

Dehydrogenation was accomplished using chloranil, the pale, yellow needles of 5-methylbenzo(ghi)fluoranthene (72) melting at 203-4°C.

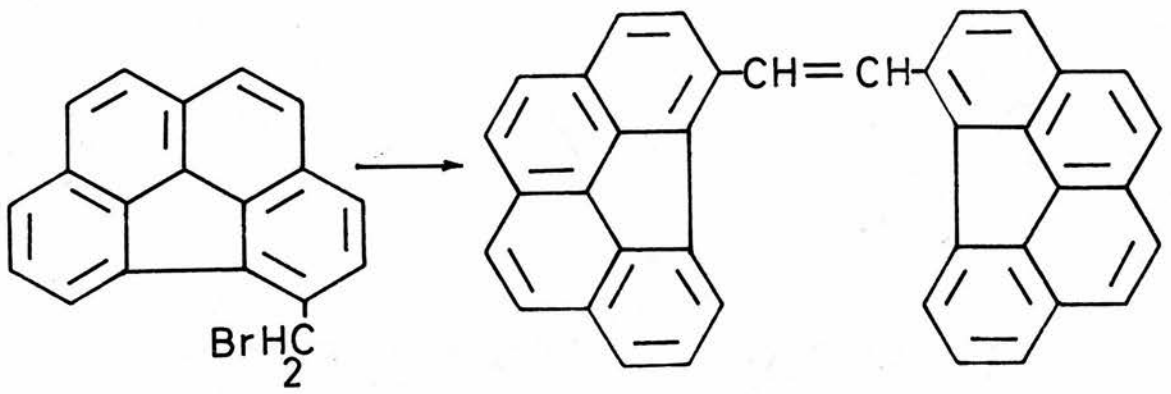


(100) (72) (101)

As in the previous synthesis, peroxide-catalysed side-chain bromination with N-bromosuccinimide proceeded smoothly, 5-bromomethylbenzo(ghi)fluoranthene (101) separating on cooling the reaction mixture.

The synthesis of coronindene had proceeded smoothly to this stage, as expected from the trial synthesis. It was also indicated that the cyanation stage which follows might prove troublesome. This is, in fact, something of an understatement- it proved impossible. Using both sodium and copper cyanide in a variety of solvents, no trace of benzo(ghi)fluoranthene-5-acetonitrile (102) was obtained.

Employing the technique of the trial synthesis - sodium cyanide in DMSO - most of the starting material was converted into the dimer 1:2-di-5'-benzo(ghi)fluoranthenylethylene (103), corresponding to that, 89, formed in the first synthesis.



(101) (103)

Unfortunately, in this second synthesis, this dimerisation was not a side-reaction to that of cyanation, but seemed to be the sole reaction.

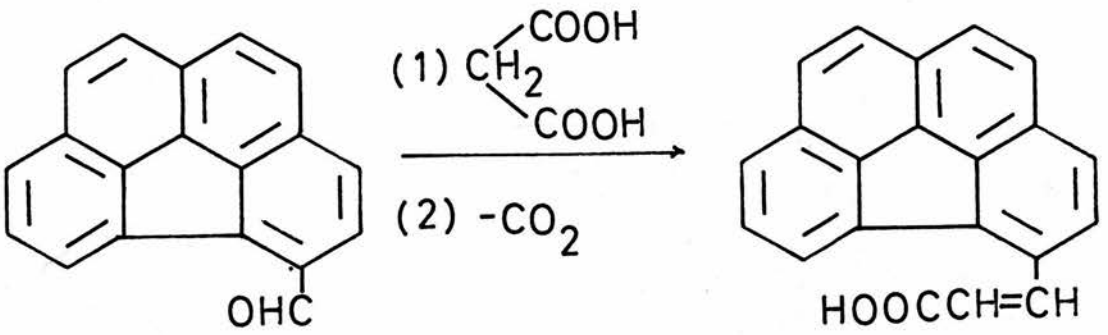
Substitution of copper cyanide for sodium cyanide gave benzo(ghi)fluoranthene-5-aldehyde (104), also obtained when pyridine was used as solvent in place of DMSO. Although the formation of aldehydes from alkyl halides with DMSO is known [71], the fact that no similar reaction was observed in the first synthesis when sodium cyanide alone was employed, but was observed in two separate reactions involving copper cyanide

in the second synthesis, would suggest that the copper is having a catalytic oxidising effect. It should, perhaps, be remembered that aldehydes can be formed from alkyl halides and copper nitrate [72]. Use of glacial acetic acid and 2-methoxyethanol as solvents with sodium cyanide resulted in return of unchanged bromo-compound.

As no success with this cyanation seemed probable, it was decided to attempt the preparation of benzo(ghi)fluoranthene-5-carboxylic acid (68) by oxidation of the 5-bromomethyl-derivative 101. This acid, an earlier preparation of which was referred to in the Introduction (p.30), could then be converted by an Arndt-Eistert reaction to the desired benzo(ghi)fluoranthene-5-acetic acid (73). Due to the insolubility of the bromide, this oxidation with potassium permanganate was frustrated, little solution of starting material being achieved with aqueous acetic acid as solvent. Starting material was recovered using acetone as solvent.

An attempt to prepare the same acid by oxidation of the aldehyde 104, appeared, from the uptake of potassium permanganate, to have proceeded beyond the desired stage, oxidation of the polycyclic nucleus most probably occurring.

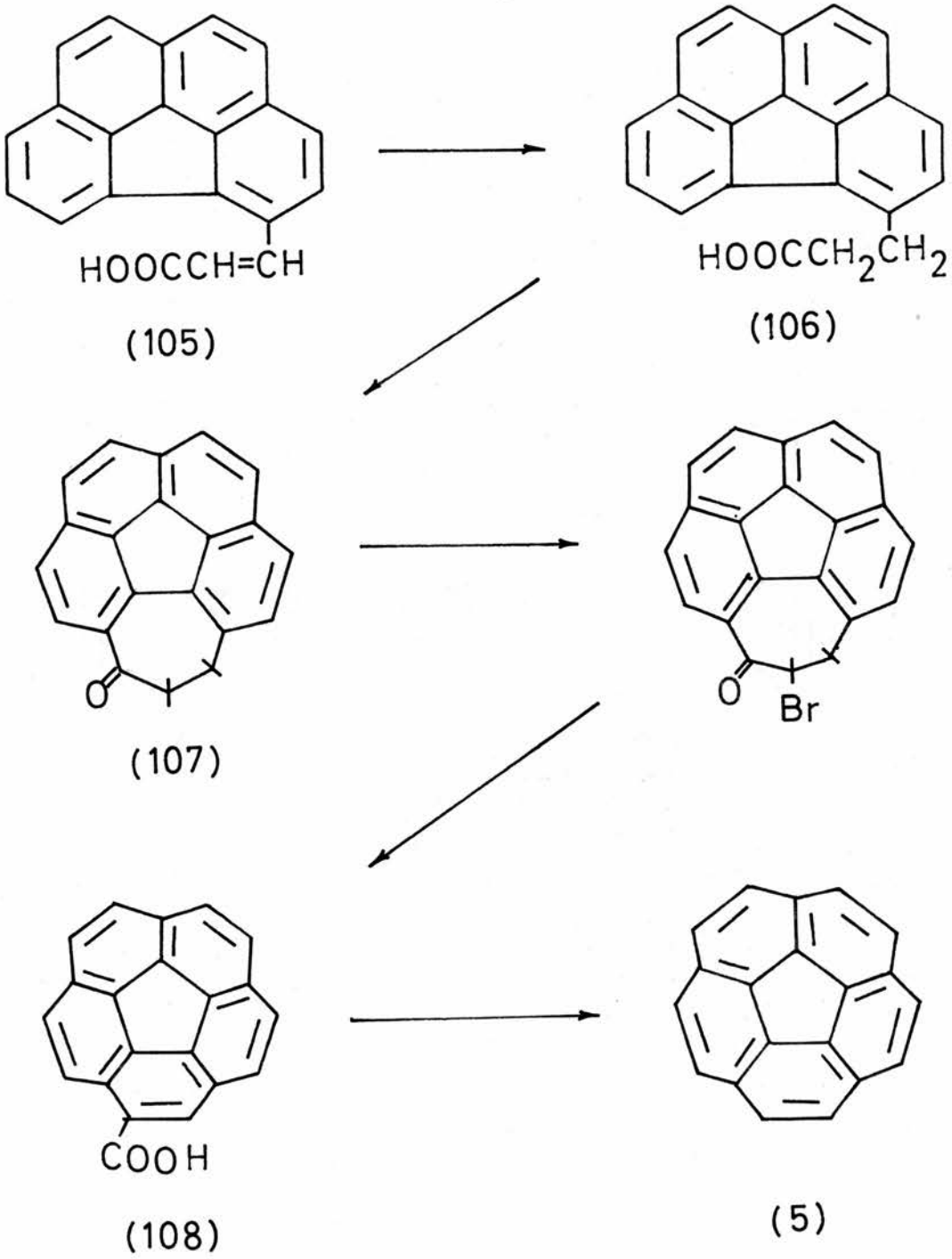
The last reaction performed in conjunction with this unsuccessful synthesis of coronindene before both material and time ran out, was condensation of the aldehyde 104 with malonic acid. On decarboxylation this gave benzo(ghi)fluoranthene-5-acrylic acid (105).



(104) (105)

A model disclosed that the trans olefinic acid - the probable isomer due to method of formation - would most probably not cyclise, but that the saturated acid 106 possessed the necessary stereochemistry to cyclise. The proposed adaption to the synthetic scheme initially proposed, was cyclisation of the acid, benzo(ghi)fluoranthene-5- β - propionic acid (106) to give a seven-membered ring ketone 107. After preferential bromination at the carbon adjacent to the ketonic group, a ring contraction by a Favorski reaction would give coronindene-1-carboxylic acid (108), which could be decarboxylated to the desired hydrocarbon 5.

This modified synthesis did not extend very far, only a very small amount of 105 being obtained.

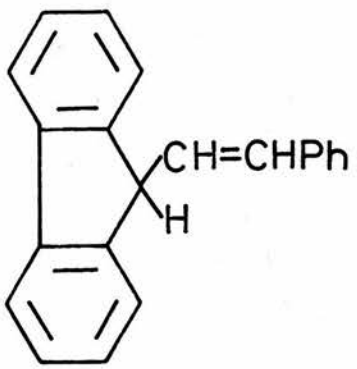


(105) (106) (107) (108) (5)

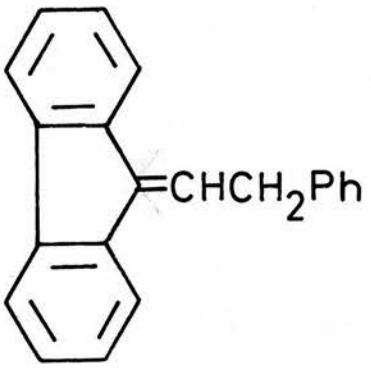
SECTION II

Outline of Contents.

This section of the thesis concerns the synthesis of the isomeric compounds β-9-fluorenylstyrene (1) and 9- β -phenylethylidenefluorene (2), together with the corresponding saturated compound, 9- β -phenylethylfluorene (3).



(1)



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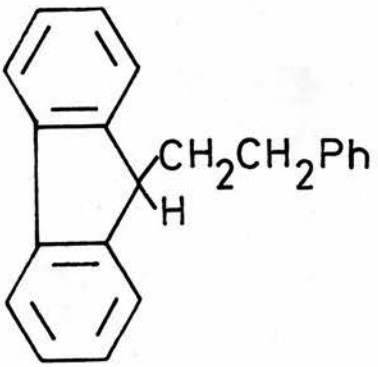


(3)

The tautomerism between structures 1 and 2 and that between other, related, isomeric compounds is also considered.

The chemistry of fluorene forms part of the Introduction to Section I of the thesis. The introduction to this section, therefore, comprises a brief outline of isomerism, with particular emphasis on prototropy, the type involved in the succeeding work.

SECTION II - PART I

Some Prototropic Systems

Introduction

A well-known phenomenon of organic chemistry is that different atomic arrangements within the molecule give different compounds. All such related compounds are termed isomers, and fall into three classes; structural, geometrical, and stereo. In this first category are included isomeric compounds which, by the transfer of a single atom, or group of atoms, undergo interconversion. This takes place by separation of the migrating atom involved as an ion, and recombination of it at an atom on the molecule other than that to which it was originally bonded. Dependent on whether the migrating ion is an anion or a cation, considerations of such isomerisations are divided into two sections, anionotropy, and cationotropy. A large section of the latter involves a proton as the migrating entity, the study of this being known as prototropy, or tautomerism.

PROTOTROPY. The phenomenon of prototropy was first evidenced in organic chemistry with the compound ethyl acetoacetate, discovered in 1863 by Geuther [74]. Between this date and the end of the nineteenth century, many more examples of this phenomenon were discovered, and two conflicting theories formulated.

The first of these was due to Butlerow [75] and Baeyer [76] who stated that each structure could have a separate existence,

but that facile interconversion could afford preparation of one from the other. Such an isomeric change in structure of one isomer immediately prior to reaction, could result in the reactions of the other isomer.

The second early theory was that of Laar [77]. In 1885-86 he drew attention to the fact that in all the cases of isomerism known at that time, the problem of ambiguity of structure was reducible to that of the position of one hydrogen atom and at least one double bond. Expressed in its simplest form, this involved the migrating hydrogen atom, three other atoms (X,Y,Z) and the two possible isomeric structures.

$$HX-Y=Z \qquad \text{and} \qquad X=Y-ZH$$

This he termed the "triad" system. Laar did not postulate the separate existence of these two structures, but, as in Kekule's oscillating theory for the structure of benzene, regarded them as the extremes in an intramolecular oscillatory process of a single substance. This he termed tautomerism.

The true picture of such isomerism is, in fact, a combination of the above two postulates. Laar was correct in that basically the structural differences are formally a question of the position of one hydrogen atom and a double bond. He was, however, wrong in his contention that only one of the possible isomers existed.

The ideas of Butlerow and Baeyer of both isomeric forms having a potentially separate existence were first substantiated by the isolation of the separate isomers of a number of β-diketones, β-ketonic esters, β-aldol esters, and a paraffinic nitro-compound by respectively Claisen, Knorr, Wislicenus, and Hantzsch towards the close of the nineteenth century.

Claisen [78] isolated separate isomers of acetyldibenzoylmethane and of tribenzoylmethane.

$$PhCOCH(COPh)_2 \quad \text{and} \quad PhC(OH)=C(COPh)_2$$

Knorr [79] separated the isomers of ethyl dibenzoyl and ethyl diacetyl succinate.

$$\begin{array}{lll} RCOCHCOOEt & RC(OH)=CCOOEt & RC(OH)=CCOOEt \\ \quad\quad | & \quad\quad | & \quad\quad | \\ RCOCHCOOEt & RCO-CHCOOEt & RC(OH)=CCOOEt \end{array}$$

Wislicenus [80] isolated the isomers of the β-aldol esters, methyl and ethyl formyl phenylacetate.

$$\begin{array}{lll} CHO & CHOH & HOCH \\ | & \| & \| \\ PhCHCOOR & PhCCOOR & PhCCOOR \end{array}$$

Hantzsch [81] separated the two isomeric forms of phenylnitromethane.

$$PhCH_2NO_2 \qquad PhCH=NO\cdot OH$$

The demonstration of the existence of separate isomeric forms, which finally disposed of Laar's oscillatory theory was the separation of the keto and enolic forms of ethyl acetoacetate. This had long been regarded as the compound giving most support to Laar's postulate as, owing to its high mobility, separation had not been achieved. This was accomplished by Knorr [82] in 1911 working at very low temperatures.

In addition, it was shown in the cases above that all of the different respective isomers would isomerise to give the same equilibrium mixture, and that any one isomer could be obtained from this equilibrium mixture by shifting the equilibrium in its favour by, for example, preferential crystallisation or distillation.

Ideas as to the mechanism of tautomerism came at the very end of the nineteenth century. The clue to this stemmed from the accumulating evidence regarding the correlation between rate of attainment of tautomeric equilibrium, and the ionising power of the solvent. Both Knorr [83] and Wislicenus [84] realised that the migrating hydrogen atom was liberated as a proton, and that bond changes took place within the anion, recombination taking place at a different atom of the molecule. General acceptance of these ideas, however, was delayed by the difficulty experienced at that time in understanding the necessary charge redistribution which must take place in the

anion. Only with the advent of the electronic theory of valency did the whole picture of tautomerism - and more widely that of anionotropy and cationotropy - fall into place.

Thus it came to be appreciated how the movement of the negative charge remaining on the anion after the separation of the migrating proton constituted a shift of the double bond, bonds themselves being electrons or regions of negative charge.

Important advances towards a fuller understanding of prototropy were made by considering the effect on mobility of the migrating hydrogen attached to different elements, and also by the systematic study of the effects of different substituents.

The first of these factors was investigated by considering the general triad system:-

$$Ar{-}XH{-}Y{=}X{-}Ar' \rightleftharpoons Ar{-}X{=}Y{-}XH{-}Ar'$$

When X and Y are, in turn, nitrogen and carbon, the four possible systems are:-

1. X and Y both nitrogen:- Diazoamino system.

$$ArNHN = NAr'$$

2. X nitrogen, Y carbon:- Amidine system.

$$ArNHCH = NAr'$$

3. X carbon, Y nitrogen:- terminally diarylated methyleneazomethine system.

$$ArCH_2N{=}CHAr^1$$

4. X and Y both carbon:- terminally diarylated propene system.

$$ArCH_2CH{=}CHAr^1$$

By considering the products of synthetic routes designed to produce the isomers separately, it was possible to gain information about the intrinsic prototropic mobilities of the systems. This correlation was carried out by Ingold and Piggott [85], who did the original synthetic work on systems (3) and (4) above; the other systems already having been investigated by Griess [86] - system (1), and by von Pechmann [87], Marckwald [88] and Wheeler and Johnson [89] - system (2).

These investigations showed, by the fact that separate synthetic routes to each possible isomer produced the same substance in systems (1) and (2), but different substances in (3) and (4), that the systems in which the migrating hydrogen is attached to a nitrogen atom are very much more mobile tautomerically than those in which it is attached to a carbon atom. This result is easily understood in terms of separation of the migrating hydrogen ion. Nitrogen, being more electronegative than carbon releases hydrogen (as a proton) more

readily, thus rendering such systems more mobile. As will be seen later in this section, the propene systems can be made to isomerise [90], but only under the influence of basic catalysts.

The second of the factors mentioned above, namely that of the effect on mobility of different substituents, was investigated by Shoppee [91] and Ingold and Rothstein [92], who showed that the greater the electron withdrawing power of a substituent, the more mobile was the system. This can be pictured as the result of electron withdrawal from the centre on which the migrating hydrogen is attached thereby facilitating the liberation of the proton.

From the above brief résumé it can be seen that the salient features of prototropy are:-

1. the position of a hydrogen atom is always involved;
2. the mobility of any tautomeric system increases with:-
   (a) the ionising power of the solvent.
   (b) the electronegativity of the centre to which the migrating hydrogen is attached.
   (c) the electron withdrawing power of substituents.

There can be no doubt that the essential mechanism involves ionisation of the migrating hydrogen atom followed by redistribution of the most negative centre on the anion, and recombination of the proton at a new position.

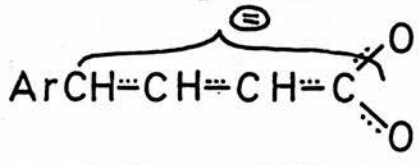
Equilibrium

Mention has already been made about the factors influencing the mobility of prototropic systems. The other important aspect of this question concerns the equilibrium of such systems. If two tautomers are allowed to equilibrate, what determines the relative proportions of the respective components? The basic principle is that at equilibrium, the thermodynamically more stable isomer will predominate.

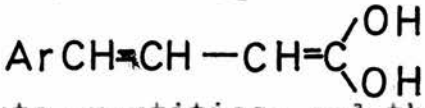
The prototropic system containing a carboxylate grouping should not, perhaps, be regarded as a true three-carbon system.

$$\underset{\lambda\ \beta\ \alpha}{ArCH{=}CHCH_2COO^{\ominus}} \rightleftharpoons \underset{\lambda\ \beta\ \alpha}{ArCH_2CH{=}CHCOO^{\ominus}}$$

Extension of the conjugation in the mesomeric anion beyond the three carbon atoms (α, β, λ.) to embrace the carboxylate groups, more formally renders this a pentad-enol system.



On acidification of the equilibrium mixture, the enol form



only exists in minute quantities, and thus, for considerations of equilibrium, such systems can be regarded as three-carbon systems with a carboxylate activating group.

The fundamental work on such systems was carried out by Kon and Linstead [96], with subsequent interpretation and correlation of their results by Ingold and Hughes [97] based

on stability due to conjugation. The two following examples will serve as good illustrations.

In the equilibrium between crotonic acid and vinylacetic acid the isomer with the double bond $\alpha\beta$ to the carboxylate group completely predominates.

$$\underset{\beta\ \alpha}{CH_3CH{=}CHCOOH} \rightleftharpoons \underset{\lambda\ \ \beta}{CH_2{=}CHCH_2COOH}$$

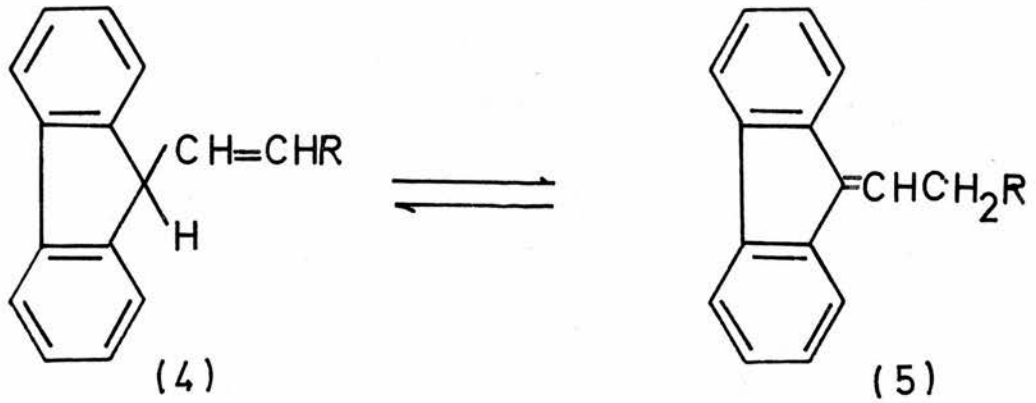
This, as might be expected, is the more thermodynamically stable isomer as a result of the conjugation between the double bond and the carboxylate group.

If, however, a phenyl group is substituted on the λ-carbon atom, the equilibrium is completely reversed, the isomer with the double bond $\beta\lambda$ to the phenyl nucleus predominating entirely.

$$\underset{\beta\ \ \alpha}{PhCH_2CH{=}CHCOOH} \rightleftharpoons \underset{\lambda\ \ \beta}{PhCH{=}CHCH_2COOH}$$

This was interpreted as indicating that the isomer with the double bond in conjugation with the phenyl nucleus is thermodynamically more stable than that in which it is conjugated with the carboxylate group.

An analogous system, i.e., one in which the double bond could conjugate with either an aryl or carboxylate substituent, is that involving β-9-fluorenylacrylic acid (4.R=COOH) and β-9-fluorenylideneproprionic acid (5.R=COOH).



(4) (5)

The preferred structure is that in which the double bond is conjugated with the fluorene nucleus as shown by Campbell et al [98].

It is of interest to examine the equilibrium of three-carbon systems terminated at either end by aryl substituents and relate the equilibrium to the relative conjugative stabilisation of these groups.

Such systems have already been discussed from the aspect of mobility, (p.74 system 4) the systematic investigation of which was carried out by Shoppee [91]. The systems examined were those shown below in which R was $\overset{+}{N}R_3$, NMe_2, OMe, I, Br, Cl, Me.

$$p\text{-}R\text{-}C_6H_4CH{=}\overset{COOEt}{\overset{|}{C}}CH_2C_6H_5 \rightleftharpoons p\text{-}R\text{-}C_6H_4CH_2\overset{COOEt}{\overset{|}{C}}{=}CHC_6H_5$$

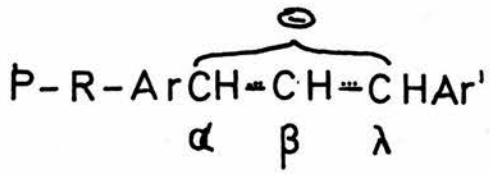
$(\alpha\beta)$ (w.r.t. the substituted ring) $(\beta\lambda)$

$$p\text{-}R\text{-}C_6H_4CH{=}NCH_2C_6H_5 \rightleftharpoons p\text{-}R\text{-}C_6H_4CH_2N{=}CHC_6H_5$$

As already stated (p.75) the mobility of such systems was shown to parallel the inductive electron-withdrawing

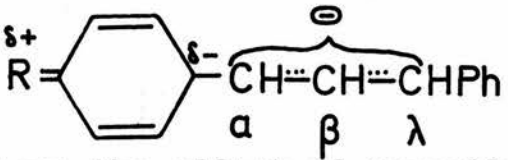
effects of the R-substituents.

The early view [99] regarding equilibrium was that this, too, should follow the same order as did mobility, the most powerful electron-withdrawing groups absorbing charge from the carbon atom (C α) of the mesomeric anion nearest to itself, thus inducing recombination of the proton at the C λ atom.



However, the arrangement of the substituents in order of decreasing amounts of the α β isomer in the equilibrium mixture is $\overset{+}{N}R_3$, NMe_2, OMe, I, Br, Cl, Me, which, on comparison with the order of decreasing -I effect, i.e., $\overset{+}{N}R_3$, Cl, Br, I, OMe, NMe_2, Me, demonstrates that this is not the factor controlling equilibrium.

An alternative idea advanced by Baker [100] was based on a realisation of the importance of the conjugative effect in controlling equilibrium. It was suggested, by the +T effect, a partial negative charge would be generated on the carbon atom of the ring to which the side-chain was attached.



This would have the effect of "repelling" the negative charge of the mesomeric anion to the carbon atom (C λ) furthest from this induced charge. This now being the most electron dense centre in the anion recombination would take

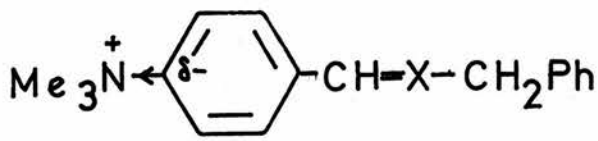
place here.

Both these explanations, however, were based on the assumption that the isomer resulting from recombination at the position of highest electron density will predominate. This, of course, is the condition of kinetic control of equilibrium and not thermodynamic control, which has already been stated as the fundamental criterion in this question. The real control of equilibrium is the relative thermodynamic stabilities of the two isomers.

Examined in this light, a qualitative explanation for the above equilibrium can be obtained, i.e., why particular isomers are more stable than others. Equilibrium amounts of $\alpha\beta$ isomer [101]:-

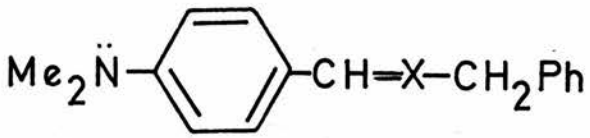
	R	NR_3	NMe_2	OMe	I	Br	Cl	Me
System	A	90	-	57	-	54	50	48
System	B	-	87	73	53	48	47	45

$R\,Me_3\overset{+}{N}$



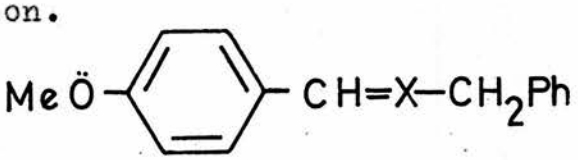
Due to the strong electron withdrawing inductive effect of the ammonium group there is a tendency for a partial negative charge to be set up at the carbon atom of the ring to which it is attached. The energy of the system will be least when this strain can be distributed over the greatest number of atoms, which it can do in the case when the double bond is conjugated $\alpha\beta$ to the ring carrying the substituent.

R = NMe_2.



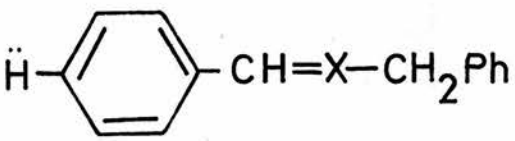
The isomer with the greatest thermodynamic stability will be that in which there is most conjugation. This is the isomer with the double bond α β to the ring carrying the substituent, the lone pair of electrons on the nitrogen, and the π electrons of the ring and double bond all being in conjugation.

R = OMe



This is analogous to the example discussed above, there being conjugation of the electrons of the oxygen with the double bond. The above examples all showed a marked predominance of the α β isomer. In the case of the halogens and methyl substituents the proportions of the isomeric forms are very nearly equal.

R = Hal.



In this case the explanation is much more difficult due to the problem of the interplay between the -I and +M effects of the halogens. Any extended conjugation due to the +M effect of the halogen could be counteracted by their -I effect. In the case of the halogen and with R=Me, the equilibrium is not sufficiently decisive to make any generalisations.

Object of the Research.

To examine qualitatively the equilibrium of some diarylated prototropic three-carbon systems.

Discussion of Results.

The prototropic system involving the isomers β-9-fluorenylstyrene (4. R=Ph) and 9- β -phenylethylidene-fluorene (5. R=Ph) affords two useful comparisons.

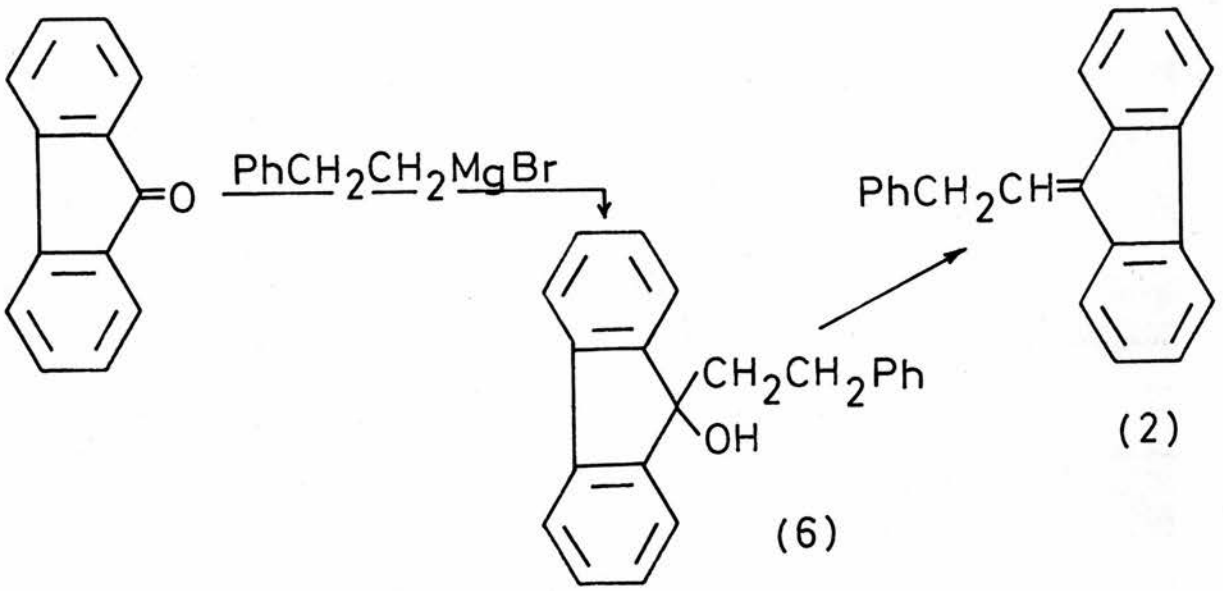
Firstly, this system is a diarylated propene system in which the extent of conjugation differs in the two isomers. This will provide a good test of the postulate that the predominant isomer is that having the lowest thermodynamic stability by virtue of greatest extent of conjugation.

In addition, a comparison may be made between this system and the analogous one already mentioned (p.77) involving β -9-fluorenylacrylic acid (4. R=COOH) and β -9-fluorenylidenepropionic acid (5.R=COOH) to compare the relative conjugating influence of the phenyl ring with that of the fluorenyl nucleus.

The two isomers β -9-fluorenylstyrene and 9- β -phenyl-ethylidenefluorene were prepared, and their base catalysed tautomerism examined by ultraviolet spectroscopy in ethanolic solutions in which sodium had been dissolved.

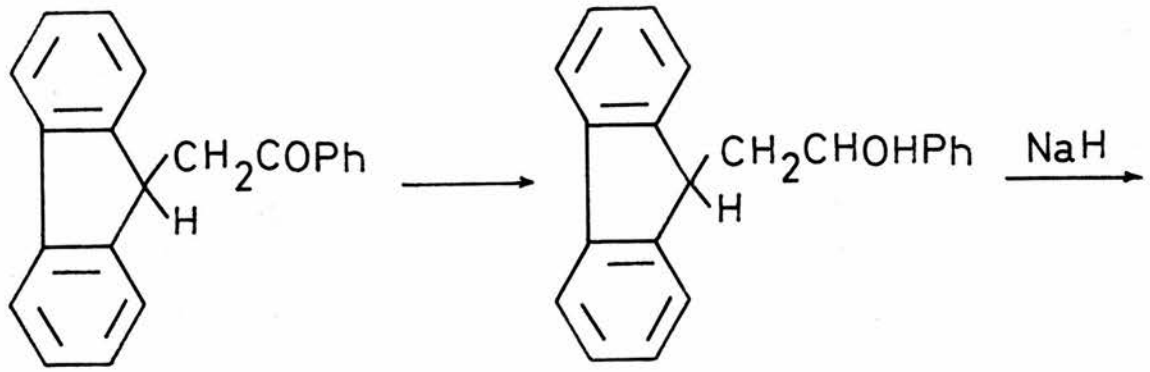
9- β -Phenylethylidenefluorene (2) was readily prepared by the dehydration of the tertiary alcohol, 9-phenylethyl-

fluoren-9-ol (6), itself obtained from fluoren-9-one by the Grignard reaction with phenylethylmagnesium bromide.



(6) (2)

After many unsuccessful attempts, β-9-fluorenylstyrene (1) was prepared by a Chugaev reaction according to the following scheme.



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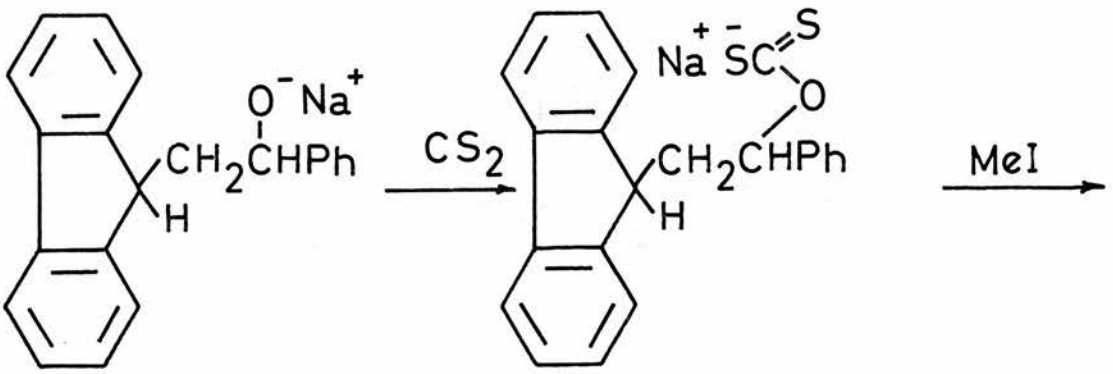
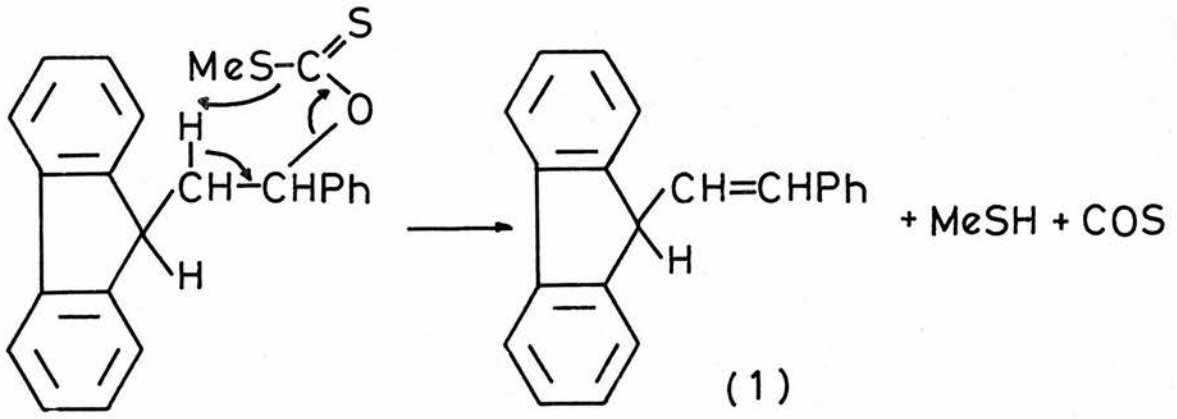
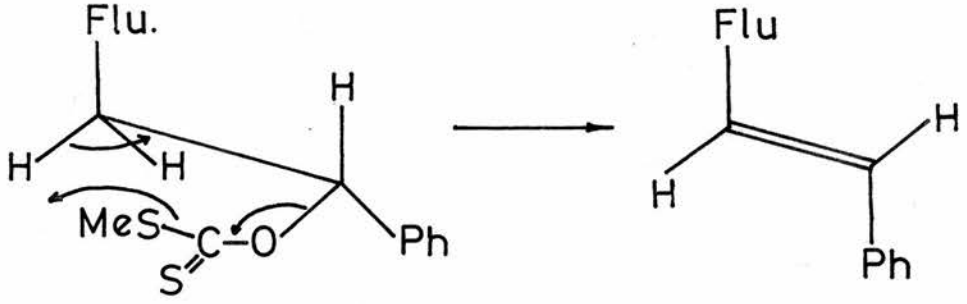




(1)

The trans β-9-fluorenylstyrene was formed, this being the isomer most likely from the stereochemistry of the cis-elimination transition state.



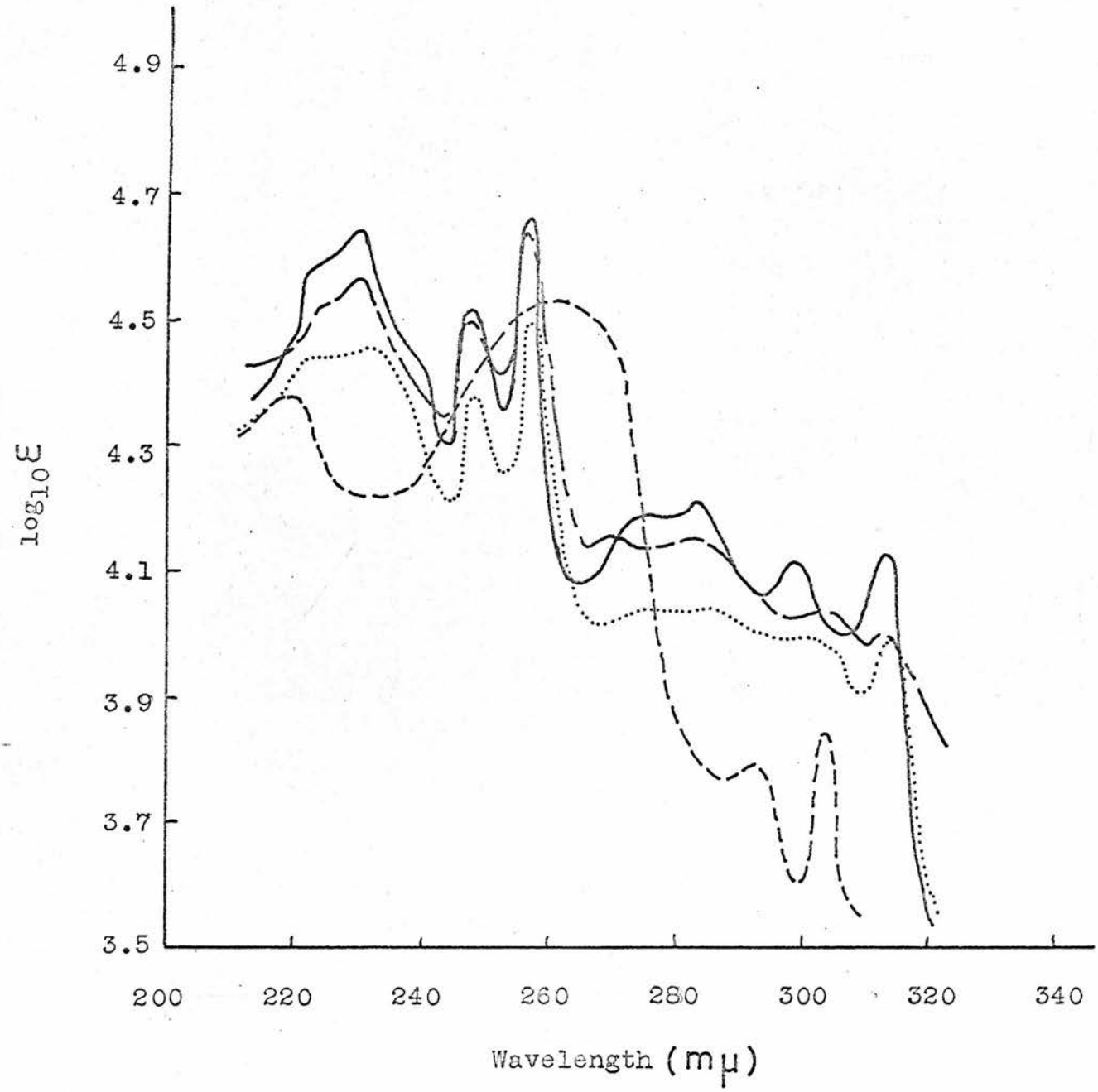
UV Spectra I.

β-9-Fluorenylstyrene (1).

Pure:- — — — With base:.....

9-β-Phenylethylidenefluorene (2).

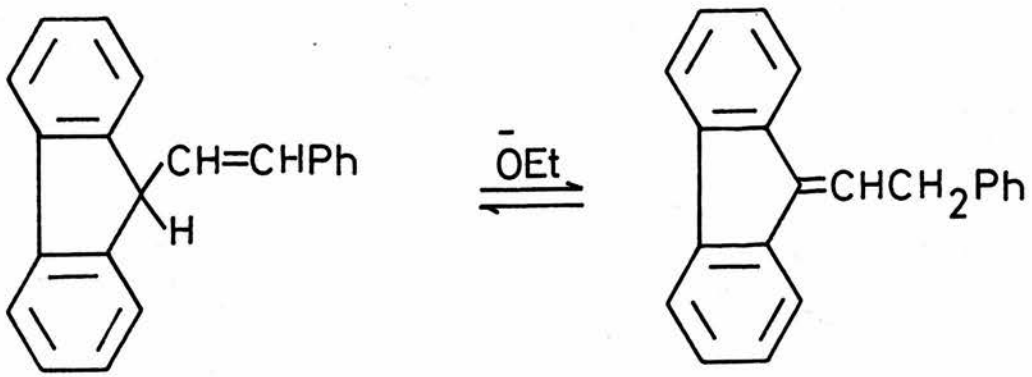
Pure:———— With base:— - - —



The trans structure for the olefine was confirmed by the IR and NMR spectra.

Base Catalysed Tautomerism.

The marked differences in the ultraviolet spectra of the fluorene and fluorenylidene structures enable any isomerisation between such structures to be observed. The ultraviolet spectra of both 9- β -phenylethylidene-fluorene and β-9-fluorenylstyrene were recorded in ethanol in the usual manner. Similar solutions were also prepared which included approximately 0·16 g/l. of dissolved sodium metal. The spectra of these solutions were taken periodically to observe any changes due to tautomerism.



The spectra of the pure compounds together with their respective base-catalysed equilibrium mixtures are shown (UV Spectra I). It is obvious that the tautomer which

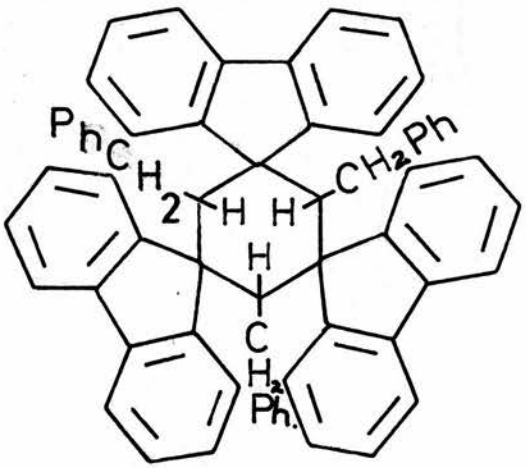
predominates markedly at equilibrium is 9- β -phenyl-ethylidenefluorene, the spectra of both equilibrium mixtures approximating closely to the spectrum of this compound. That a small amount of β-9-fluorenylstyrene is present can be seen from the diminished intensities of the various maxima.

The rates at which the respective equilibria were achieved also provide additional evidence for the greater stability of the fluorenylidene structure. The spectrum of 9- β -phenylethylidenefluorene plus base showed no detectable change for many days, the spectrum shown being that recorded after 12 days. The spectrum of β-9-fluorenyl-styrene, taken within 5 minutes of making up the solution, underwent no further change, even when kept for 2 hours.

This considerable difference, although qualitative, in the rates of achieving equilibrium is in agreement with two factors. The first being that the more mobile tautomer prototropically will undoubtedly be β-9-fluorenylstyrene, owing to the greater acidity of the hydrogen on the 9-position of fluorene [22]. Once ionisation is achieved, however, the rate of establishment of equilibrium is dependent on the relative stabilities of the two tautomers, the very rapid change from the fluorenyl to the fluorenylidene structure substantiating the greater stability of the latter structure.

Attempts to obtain 9- β -phenylethylidenefluorene from β-9-fluorenylstyrene by conversion with sodium ethoxide

were unsuccessful. Conversion using ethanolic potassium hydroxide was also attempted. On warming, separately, both 9- β -phenylethylidenefluorene and β-9-fluorenylstyrene in ethanol containing dissolved potassium hydroxide, solid material separated from the solution. This solid, which contained both fine needles and prisms, melted over the range 230-240° C, and gave a mixed melting-point depression with bifluorenyl, m.p. 242-4°C. This solid was not completely identified, but has been tentatively assigned as being a mixture of the possible isomers of the "trimer" 1:3:5-tri(9-spiro-fluorene)2:4:6-tribenzylcyclohexane on the following evidence.



Analysis. The analysis for carbon and hydrogen and molecular weight gives a hydrocarbon in close agreement with the proposed structure.

IR-Spectrum. The IR-spectrum shows phenyl and fluorene characteristic peaks in the aromatic C-H. o.o.p. deformation region 760-690 cm^{-1}.

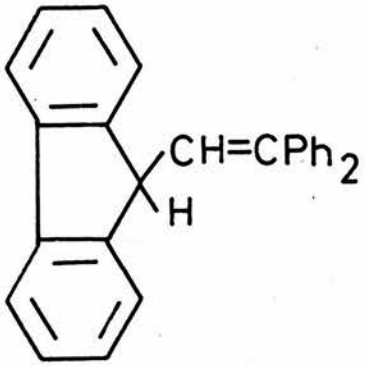
UV-Spectrum.

"Cyclohexane derivative"	208.5(5.20)	258,0(4.91)	300.5(4.24)	306.0(4.1)
Spiro-1-(9-fluorenyl)-2-phenylcyclopropane (35)	211.0(4.77)	270.0(4.25)	293.0(3.93)	304.0(3.93)
9- β-phenylethyl-fluorene (3)	210.5(4.68)	267.3(4.25)	291.5(3.76)	302.5(3.93)

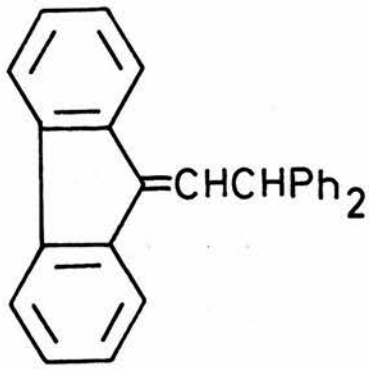
NMR-Spectrum. The NMR-spectrum, which was not satisfactory due to difficulty in solubility, gave an aromatic complex at τ 1.9-2.9, and a signal at τ 4.85.

It should, perhaps, be stressed that the change in the ultraviolet spectrum of β-9-fluorenylstyrene in base cannot be due to formation of this trimer. The spectral change was from a fluorenyl structure to a fluorenylidene structure, the spectrum of the trimer showing a fluorenyl structure.

The second prototropic system examined was that involving 1:1-diphenyl-2(9-fluorenyl)ethylene (7) and 1:1-diphenyl-2(9-fluorenylidene)ethane (8).



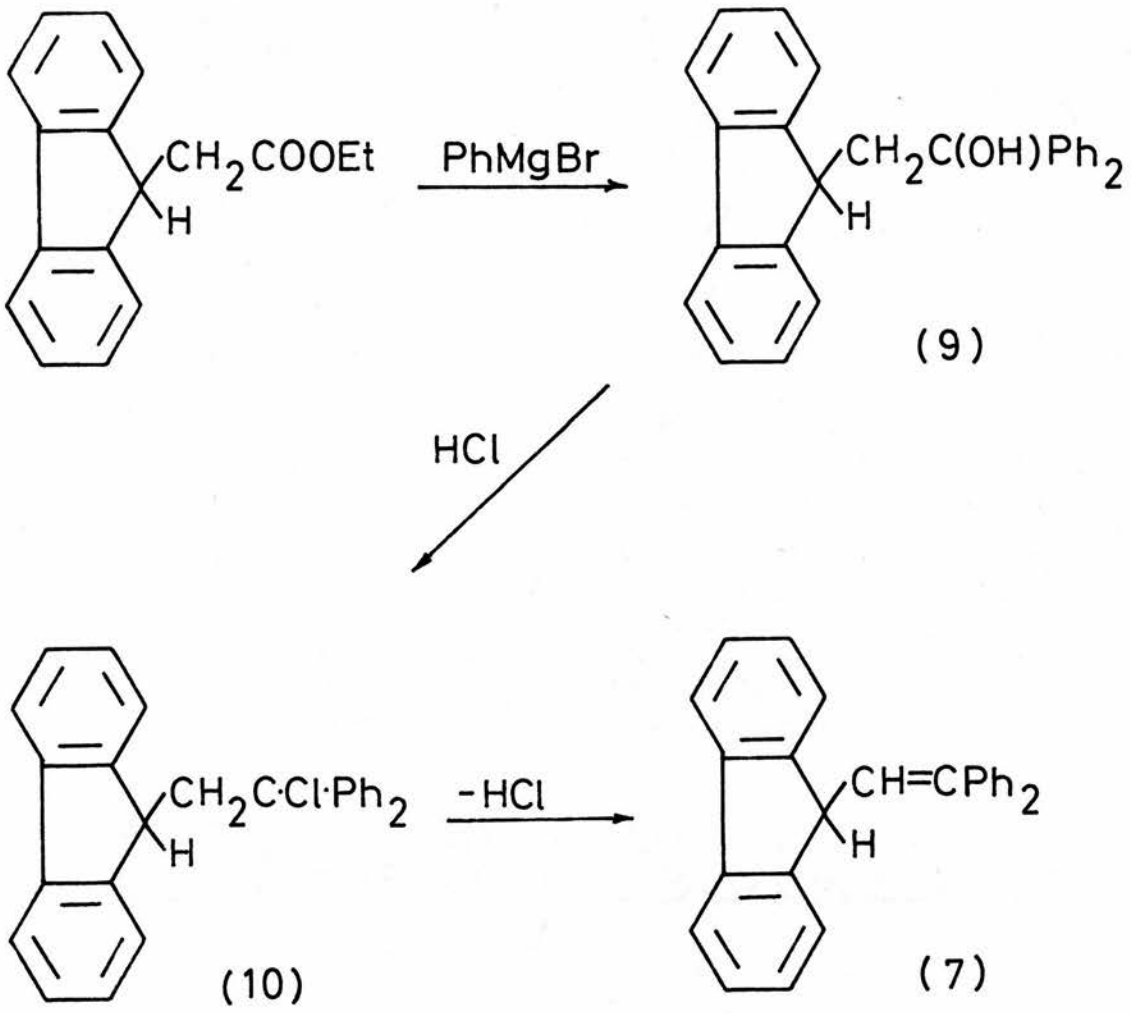
(7)



(8)

This system was chosen to investigate qualitatively the equilibrium between structures in which the double bond can conjugate with either the fluorene or two phenyl nuclei. The first reported preparation of 7 was by Schlenk and Bergmann [103] with a melting point of 112°C. Kuhn, however, later claimed [41] that, in fact, it was the other isomer 8 that had been prepared. Kuhn himself prepared 8 by a different route and reported a melting point of 105-7°C. Both of these synthetic methods were repeated.

Schlenk and Bergmann's synthetic scheme was as follows:-



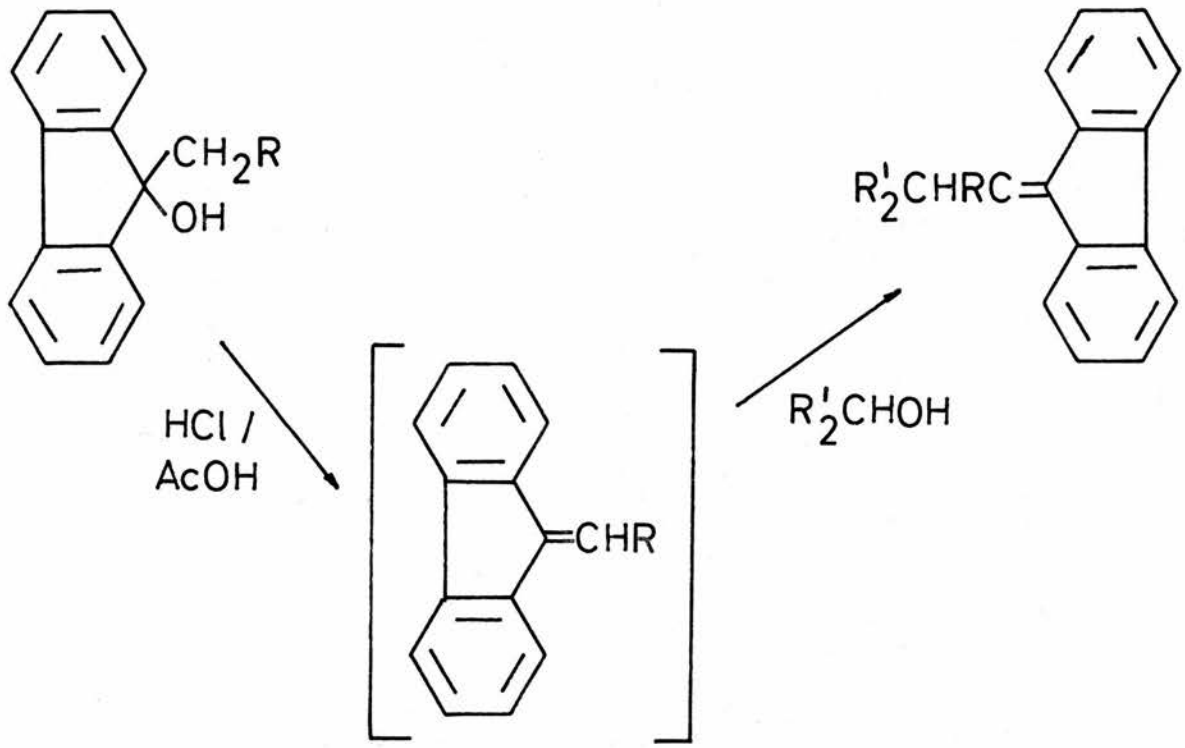
According to the above workers [103]..... "the carbinol 9 was suspended in a little ether, which, on cooling and saturating with hydrogen chloride gas, the solid firstly dissolved, and suddenly, what was probably the chloride 10, separated as a heavy crystalline precipitate. The ether was expelled and the residue boiled with pyridine for 3 hours, diluted with sulphuric acid ....."

This work was repeated as described, except that the "heavy crystalline precipitate" was isolated. This compound was 7, the hydrogen chloride effecting the more likely dehydration of the carbinol 9 than formation of the chloride. It was identical in all respects with the products of dehydration of 9 with both 90% formic acid and thionyl chloride, the melting point being 150-151°C.

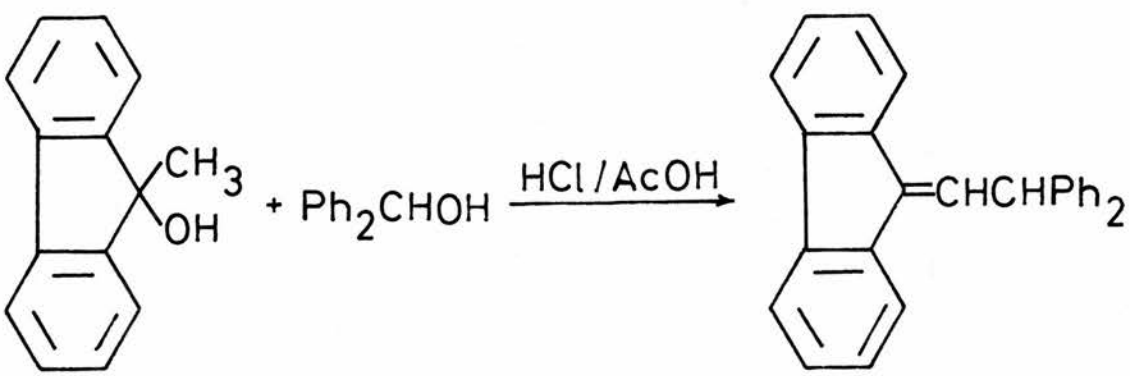
To determine what, in fact, Schlenk and Bergmann had obtained, 7 was treated as described with pyridine, a solid being obtained which melted at the value given by Schlenk and Bergmann viz. 112°C. Both the UV and NMR spectra of this material showed it to be a mixture of 7 and 8, more careful crystallisation giving separation of the two isomers in a still impure state.

Thus, Schlenk and Bergmann, without realising it, had prepared 7 as they intended, but, by continuing without isolating this product, the treatment with pyridine gave them a mixture of the two isomers; a mixture which, by coincidence, has almost the same melting point as 8 (see below).

The compound 8 was prepared exactly by the method described by Kuhn [41], who was utilising a method first reported by Wawzonek and Dufek [40] which may be generalised as shown below.



The reaction of 9-methylfluoren-9-ol, from the Grignard reaction of methylmagnesium iodide and fluorenone, with benzhydrol gave 8.



(8)

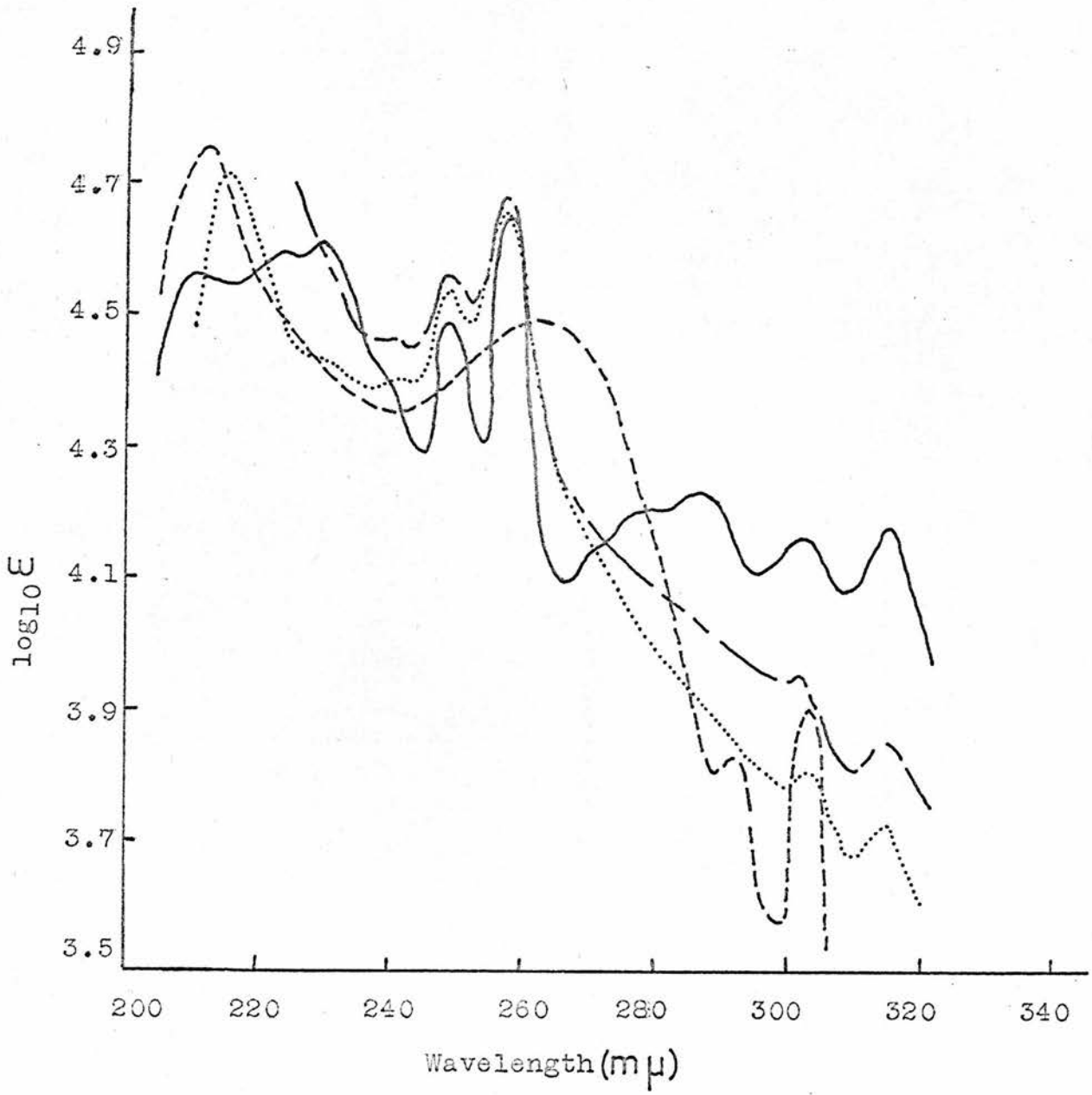
UV Spectra II.

1:1-Diphenyl-2-(9-fluorenyl)ethylene (7).

Pure: – – – – – – – With base: ·····

1:1-Diphenyl-2-(9-fluorenylidene)ethane (8).

Pure: ——————— With base: —— – – ——



Although Kuhn reports this compound as having a melting-point of 105-7°C., the melting-point obtained, constant after three crystallisations, was 113°C. The NMR and UV spectra show that it is a pure compound. On treatment with pyridine similar to that on 7, 8 gave a material m.p. 100-2°C., which was shown by NMR-spectroscopy to be a mixture of the two isomers. This compares with the material m.p. 112°C. obtained from 7. Obviously the proportions of the isomers differ in the two mixtures, this probably being due to differences in solubility, rather than differences in the equilibria.

Base Catalysed Tautomerism.

It is possible to isomerise both 7 and 8, as is evident from the results with pyridine already mentioned. As with the first prototropic system discussed, the isomerisation with sodium ethoxide was examined by UV-spectroscopy. UV spectra of 7 and 8 were recorded in the usual manner, as were identical solutions containing approximately 0.16 g/l. of dissolved sodium metal. The spectra of the pure compounds and of their respective equilibrium mixtures are shown (UV spectra II). It is apparent from this comparison that in both equilibrium mixtures, both isomers are present, with 8 predominating. Again some information can be obtained from the qualitative rates at which tautomerism took place. As in the first system discussed, the isomer with the double

bond $\beta\lambda$ to the fluorene nucleus isomerised more quickly than that with the double bond $\alpha\beta$ to the fluorene. In fact, after 2 days, when the spectrum of the $\beta\lambda$ isomer had altered quite appreciably (the spectrum shown is after 6 days), the spectrum of the $\alpha\beta$ isomer had shown very little detectable change. The spectrum shown of the $\alpha\beta$ isomerised mixture was that after 2 days at a concentration of base five times that of the $\beta\lambda$ isomerised mixture. These results again involve the two factors (p.86) (i) the $\beta\lambda$ isomer is the more mobile (acidity of the 9-hydrogen of fluorene) and (ii) the $\alpha\beta$ isomer is the more thermodynamically stable.

When these very approximate times are compared with those of the first prototropic system considered, it is seen that change in the $\alpha\beta$ isomers took place more slowly when one phenyl group terminated the side chain, but that change in the $\beta\lambda$ isomers took place very much more quickly with one terminal phenyl group. These observations are elaborated on below.

The third prototropic system examined was that involving the isomers:-

1:1:3-triphenylpropene-1(11) [106] and

1:3:3-triphenylpropene-1(12) [107].

$Ph_2C{=}CHCH_2Ph$ (11) $Ph_2CHCH{=}CHPh$ (12)

This system is of interest as, not only is it a terminally arylated three-carbon system, but its constituent isomers

embody the differing features of the side-chains in the two 9-substituted fluorene systems already discussed, and should thus afford correlation of the results from these systems.

Compounds 11 and 12 have very similar ultraviolet spectra, and thus investigation employing this technique was not contemplated. The two isomers were separately treated with ethanolic potassium hydroxide and the products examined by IR and NMR-spectroscopy.

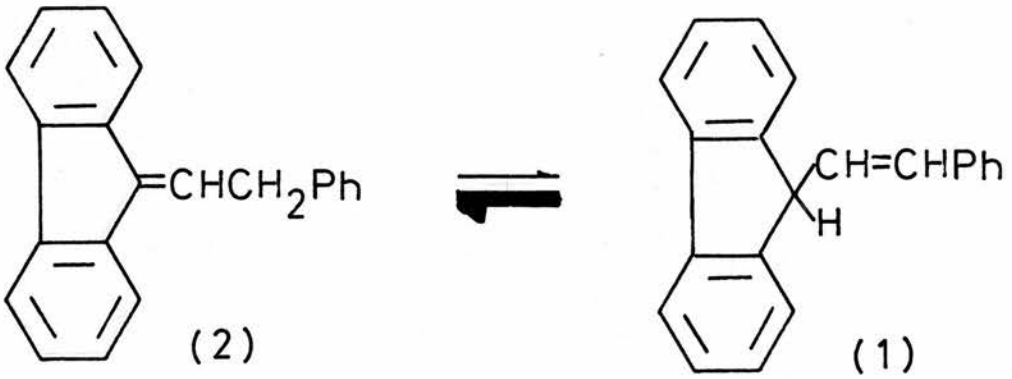
The products of isomerisation in both cases were initially oils which crystallised with difficulty, the melting points of both these solids being 40-41°C. The IR spectrum of both of these products were identical and very similar to that of 11. The most noticeable difference between these spectra and the spectrum of 12 was the absence of the strong trans olefinic CH. o.o.p. deformation band. The NMR data provides additional clear evidence for the preference of 11, the isomer in which the double bond is conjugated with two phenyl groups. The spectra of the oils obtained by alkali treatment are very similar to the spectrum of 11, no trace of 12 being detected.

Both of the solid isomerisation products and 11 itself are unstable, liquifying on standing. The formation of a hydroperoxide is indicated by the colouring of starch iodide paper and the appearance of a band in the IR spectrum assignable to the O-O-H. st.

The above results may be summarised:-

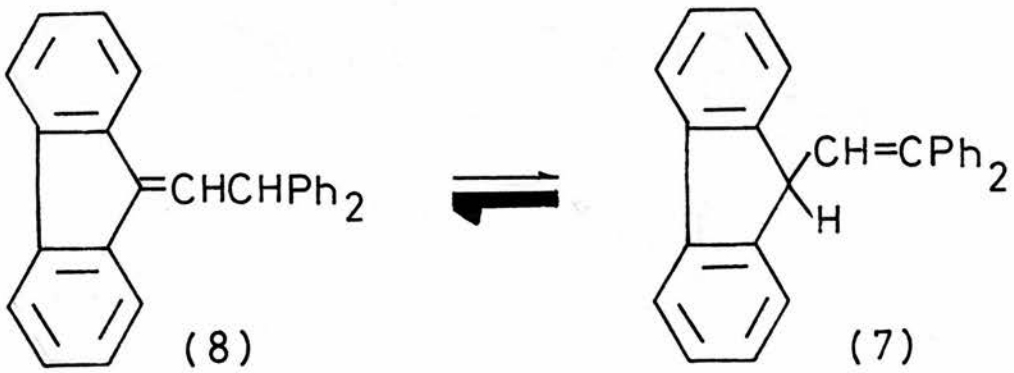
System. $\alpha\beta$ isomer. $\beta\lambda$ isomer.

A.



(2) (1)

B.



(8) (7)

C. $Ph_2C{=}CHCH_2Ph$ $\rightleftharpoons$ $Ph_2CHCH{=}CHPh$

(11) (12)

As would be expected from the absence of any very powerful internal activating influence of the nature discussed in the Introduction, none of these systems is so mobile, or has one tautomer so much more stable that it

alone exists to the exclusion of the other form. In fact, all the above six compounds have separate existence, although 11 is oxidised to a hydroperoxide on standing.

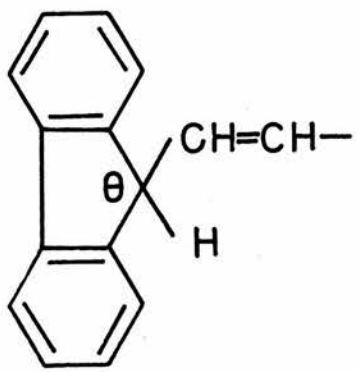
In all three systems the preferred structure is that with the double bond $\alpha\beta$ to the two-ring terminal group. In addition, it can be said that the $\alpha\beta$ form 2 displayed greater stability relative to the $\beta\lambda$ form 1 in system A than did the $\alpha\beta$ form 8 relative to the $\beta\lambda$ form 7 in system B. A phenyl group, by comparison with e.g., a keto-group, has a slight prototropic activating effect, and thus system B, with two phenyl groups in the side-chain, should be slightly more mobile than system A. The difference, however, between prototropic mobility and the rate of establishment of equilibrium must be borne in mind. The rate of establishment of equilibrium, once ionisation is achieved, depends solely on the relative thermodynamic stabilities of the two tautomers. The greater the difference, the faster will equilibrium be established. As stated, 7 should be slightly more mobile than 1. But equilibrium was achieved much more rapidly, and to a very much greater extent towards the $\alpha\beta$ form, in system A. This clearly demonstrates the greater relative preference for the $\alpha\beta$ form in system A than in system B.

The explanation of these results in terms of thermodynamic stability is readily seen from a qualitative examination of the factors influencing this stability.

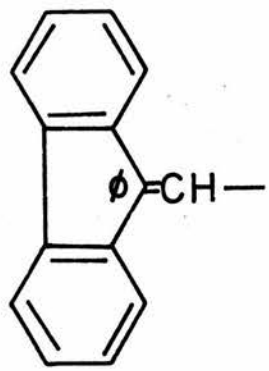
The preferred structure is that which has the lower thermodynamic energy. Differences in the thermodynamic energy between any two isomers will be due to two factors, viz. sigma bond energy and π-electron energy.

Sigma-bond energy. Sigma-bond energy strain energy will arise when sigma bond angles are caused to deviate from the unstrained sp^3 and sp^2 hybridisation angles of 109° 5' and 120° respectively.

Examination of systems A and B show that sigma bond strain differences between the isomers will occur at the 9-carbon atom of the fluorene nucleus which is involved in the two isomers both in the sp^3 hybridised state (13. fluorenyl structure) and in the sp^2 hybridised state (14. fluorenylidene structure).



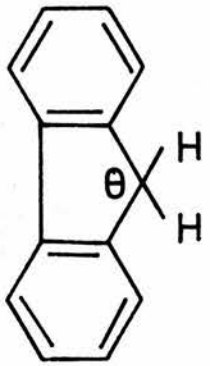
(13)



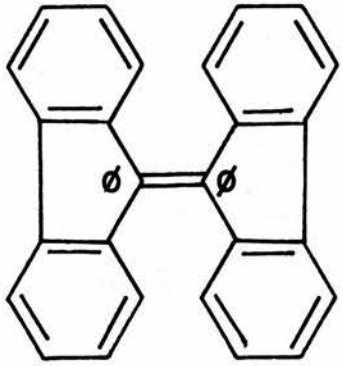
(14)

In 14, the unstrained angle ϕ would be 120°, while in 13, the unstrained angle θ would be 109° 5'. By comparison with closely analogous structures whose molecular dimensions are known, an estimation of the extent of any sigma bond energy strain energy can be obtained.

The structures of fluorene (15) [108], and bifluorenylidene (16) [109], are known accurately from X-ray diffraction analysis.



(15)



(16)

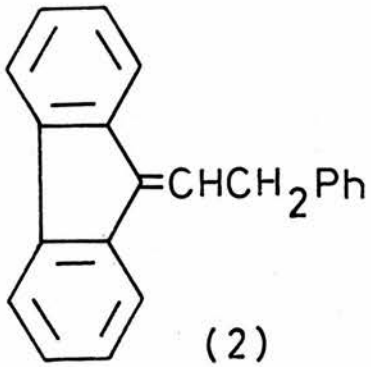
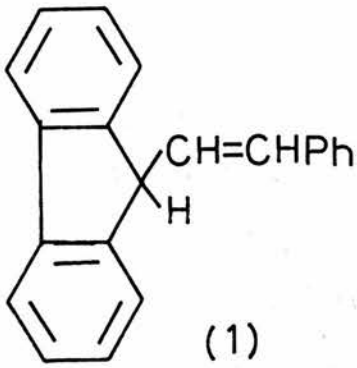
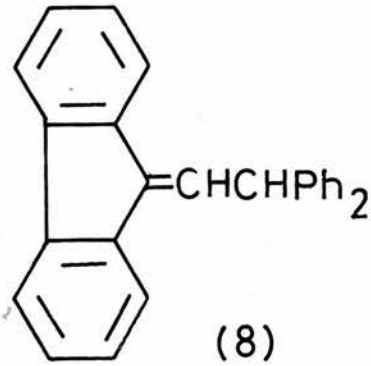
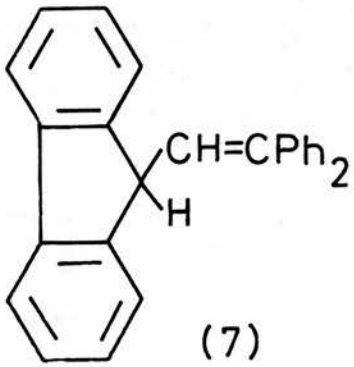
The angle θ in fluorene was found to be 105° 38', and the angle ϕ in bifluorenylidene 118°. This involves a compression of the unstrained sp^3 and sp^2 hybrid angles by 3° 27' and 2° respectively. From these figures two points may be made. Firstly, what sigma bond energy strain energy does result from these departures from the unstrained angles will be small, as the amount of compression itself is small. Secondly, the magnitude of the strain will be of very much the same order in both the fluorenyl and

fluorenylidene isomers, and, hence, no appreciable difference in the energy between them is to be expected from the sigma-bond strain considerations.

The second factor involved in determining the thermodynamic energy is the energy of π-electron delocalisation.

Bonding takes place between two atoms to form a molecule because the energy of the molecule is lower than that of the isolated atoms. This results from the fact that neither of the bonding electrons is identified with either of the nuclei in particular, but has the "freedom of access" to both nuclei. Extending this picture to conjugated systems, the greater number of nuclei to which the bonding electrons have freedom of access, the lower the energy and the greater the stability i.e., the greater the extent of conjugation, the greater the stability.

In the three prototropic systems under discussion, the extent of π-electron conjugation will provide a qualitative guide to the relative energies of the isomers. The greater the number of π-electrons in conjugation, the lower the thermodynamic energy of the isomer, and the more it will tend to predominate at equilibrium.

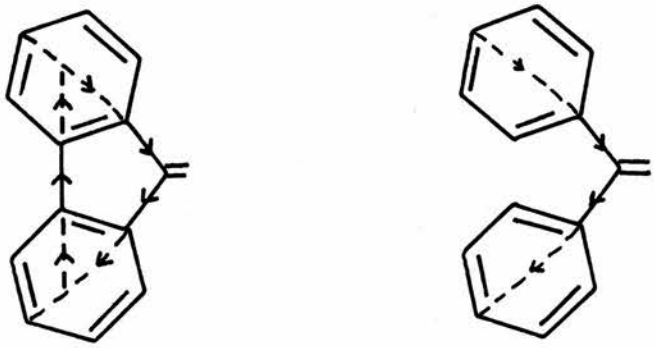
System.	αβ isomer.	βλ isomer.
A.	 (2)	 (1)
	14 π-electrons.	⩽ 8 π-electrons.
B.	 (8)	 (7)
	14 π-electrons.	< 14 π-electrons.
C.	$Ph_2C{=}CHCH_2Ph$ (11)	$Ph_2CHCH{=}CHPh$ (12)
	< 14 π-electrons.	⩽ 8 π-electrons.

The maximum conjugation between π-electron systems occurs when the respective systems are coplanar. In the event of their not being coplanar, conjugation still occurs, but to a diminished extent. Due to the planarity of fluorene [108], the conjugation in the fluorenylidene structures, 2 and 8 will involve 14 π-electrons with no possibility of

a reduction in this by loss of coplanarity due to rotation of the phenyl group, the conjugation then being proportional to the cosine of the angle between the planes of the π-electron systems involved. Thus the extent of conjugation in 1 may be described as $\leqslant 8$ π-electrons. By applying these criteria to the other isomers, the respective extents of π-electron conjugation can be similarily expressed.

In structures 7 and 11 which involve a diphenylmethylene entity, the theoretical maximum conjugation involves 14 π-electrons assuming coplanarity of the two phenyl groups and the double bond. This is almost certain not to be the most stable configuration due to steric interaction of the two α-hydrogen atoms of the phenyl nuclei. Thus the extent of conjugation can best be expressed as < 14 π-electrons.

An additional comparison of the conjugation in fluorenylidene and diphenylmethylene structures comes from considering the electronic pathways shown below.



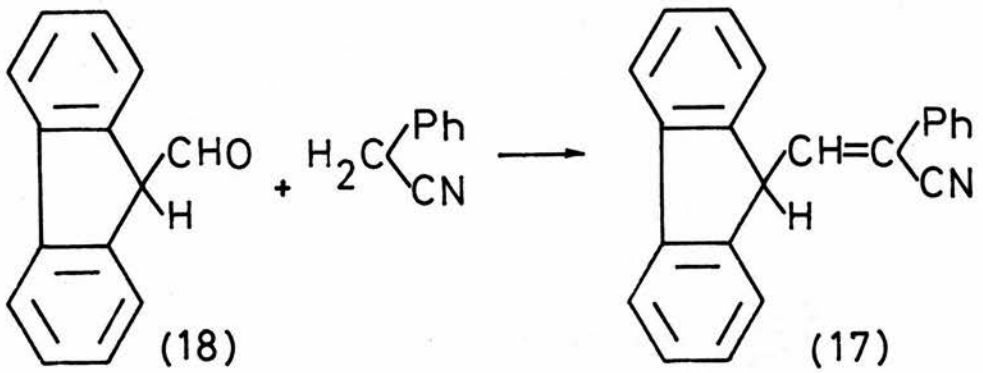
From this can be seen, that even if the diphenylmethylene entity could achieve coplanarity, the extent of conjugation would still be less than that of fluorenylidene, due to the extra linkage between the two six-membered rings in the latter.

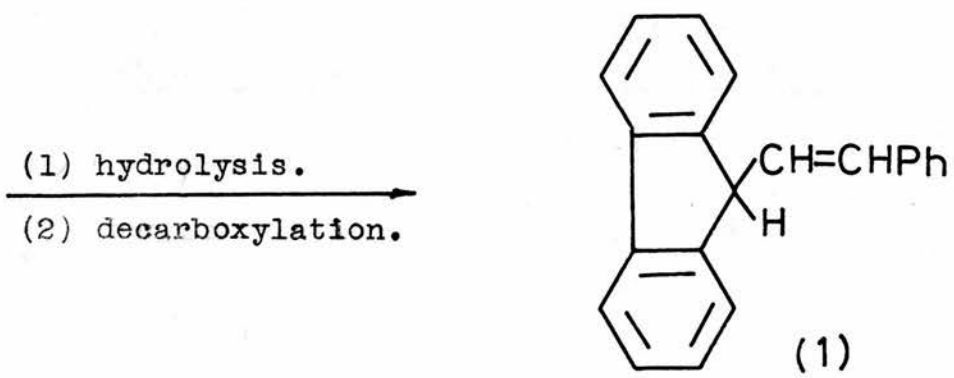
A comparison of the extent of conjugation existing in the respective components of these prototropic systems gives a very good qualitative explanation of the results found. In all three cases the $\alpha\beta$ isomer is the more extensively conjugated; in agreement with the predominance of this form at equilibria. In system A the very rapid isomerisation of the $\beta\lambda$ form to the $\alpha\beta$ form and the almost complete predominance of the latter at equilibrium in comparison to the other two systems, is explained by the difference in extent of conjugation between the isomers being greatest in system A.

SECTION II - PART II

Attempted Syntheses of β-9-fluorenylstyrene

β-9-Fluorenylstyrene (1) was first reported by Craig[110] as having been prepared by the hydrolysis and subsequent decarboxylation of α-phenyl-β-9-fluorenylacrylonitrile (17), obtained by condensing 9-formylfluorene (18) and benzyl cyanide.





The melting-point of 1 was reported as 242-4°C.

On repetition of this work, the same unstable solid which Craig assumed to be the nitrile 17 was obtained.

Alkaline hydrolysis of this solid gave as the main product, fluorene, together with a little phenylacetamide, fluorenone, and a compound m.p. 242-4° C., a mixed melting-point of this last substance with bifluorenyl (20) giving no depression. A mixed melting-point of Craig's compound m.p. 242-4° C., with bifluorenyl also showed no depression.

The unstable solid mentioned above resulted from treatment with methanol of the red-oil first obtained. Examination of the IR spectrum of this solid - an infrared spectrophotometer was not available to Craig - showed no evidence of either cyano- or phenyl-group absorptions. In addition, the infrared spectrum of the red-oil was almost identical with the infrared spectrum of 9-formylfluorene.

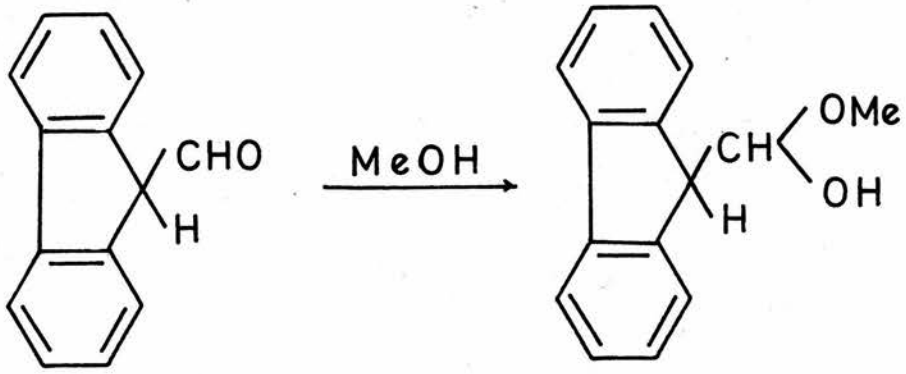
These indications that the initial condensation between 9-formylfluorene and benzyl cyanide had not taken place, suggested another experiment with the benzyl cyanide omitted. When 9-formylfluorene was boiled in ethanol containing dissolved sodium, the solution immediately went red in colour, and, on working-up as before, a red-oil was obtained, having an IR spectrum identical to that of the red-oil obtained initially, and identical with that of 9-formylfluorene. Treatment of this oil with methanol gave the same unstable solid obtained before.

A comparison of the infrared spectrum of this solid with the spectrum of the red-oil from which the solid was obtained on treatment with methanol, made an interesting study. Whereas, the spectrum of the red-oil, and of 9-formylfluorene, contains two strong absorption peaks at 1710 cm^{-1} and 1675 cm^{-1},

the spectrum of the solid shows no trace of absorption in these regions. The other features of the spectrum of this solid are an absorption at 3020 cm^{-1}.(hydroxyl OH_{st}) and a strong absorption at 1135 cm^{-1}. (ether $C-O_{st}$). This above combination of evidence indicates that the red-oil was very largely 9-formylfluorene, which on treatment with methanol, forms the hemiacetal 19.

There is evidence in the literature that equimolecular quantities of aldehydes and alcohols interact in solution to form hemiacetals. Attempts to isolate the hemiacetals lead to decomposition into the constituent aldehydes and alcohols [111]. There is also cryoscopic [112] and infrared [113] data in support of such hemiacetal formation. The infrared evidence mentioned above is in agreement with these latter data. It should be noted, however, that the aldehyde, chloral, gives, with ethanol, a hemiacetal which can be isolated.

The solid obtained in our experiment is unstable, almost immediately after isolation, a yellow oil beginning to form on the surface of the material. The compound, however, can be obtained as very fine white needles on recrystallisation from methanol, an analysis of which was carried out immediately. The compound analysed correctly, both in carbon, hydrogen and methoxyl content for the hemiacetal 19 of 9-formyl-fluorene with methanol.



(19)

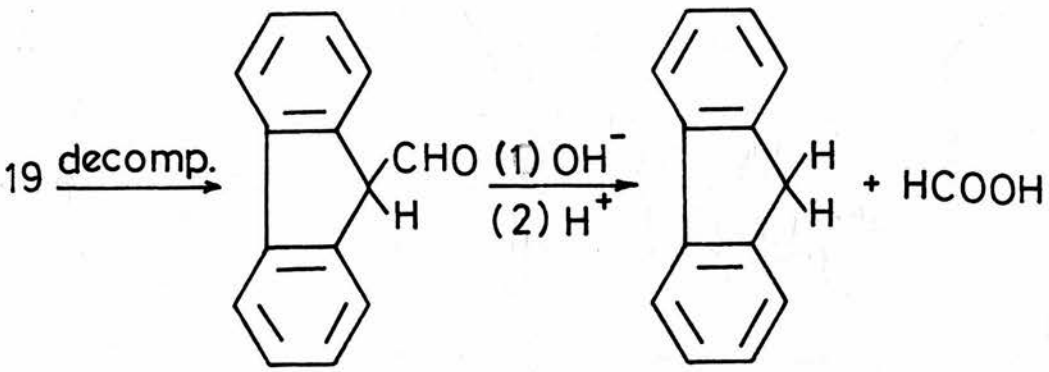
In solution, the hemiacetal tends to decompose into 9-formylfluorene and methanol, as shown by the NMR spectrum, which contains signals, varying in successive spectra, assignable to the protons of the hemiacetal, 9-formylfluorene, and methanol. Attempts to recrystallise the hemiacetal from other solvents resulted in a similar decomposition, the methanol being driven off, leaving a similar red-oil as before, which, on treatment with methanol, once again gave 19. The hemiacetal could not, however, be obtained by similar treatment of 9-formylfluorene with methanol.

The hemiacetal formed the same 2:4-dinitrophenylhydrazone as did freshly made 9-formylfluorene, resulting from decomposition into 9-formylfluorene and methanol, either spontaneously or by the catalytic action of the concentrated hydrochloric acid

added in the preparation of the hydrazone.

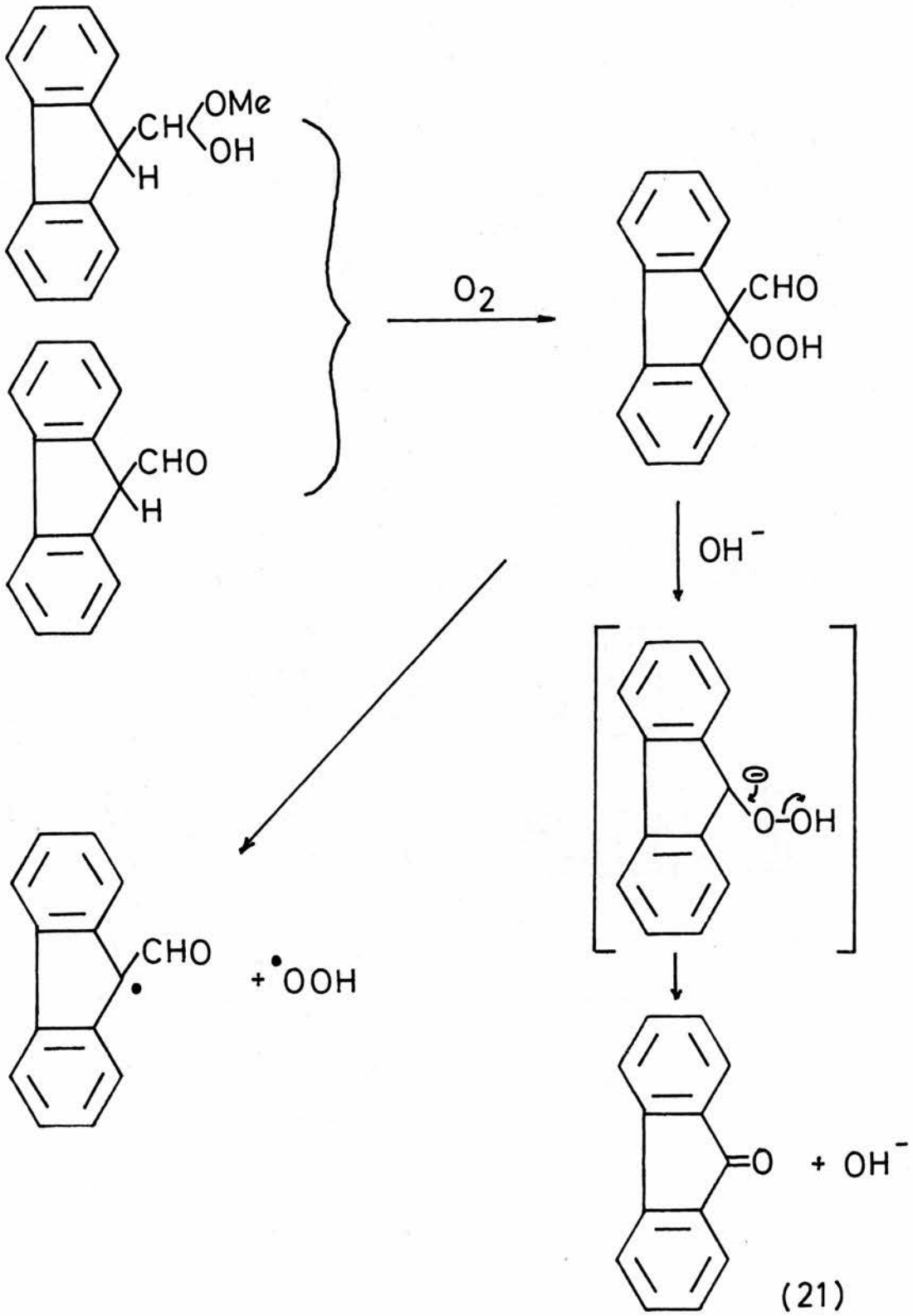
The IR spectrum of decomposing hemiacetal showed a strong absorption at 1710 cm^{-1}. ($C::O_{st}$) indicative of the presence of 9-formylfluorene in the decomposed oil.

The above-mentioned formation of fluorene by the alkaline hydrolysis of the hemiacetal is thus seen as the reverse of the condensation between fluorene and ethyl formate employed in the preparation of 9-formylfluorene [36].

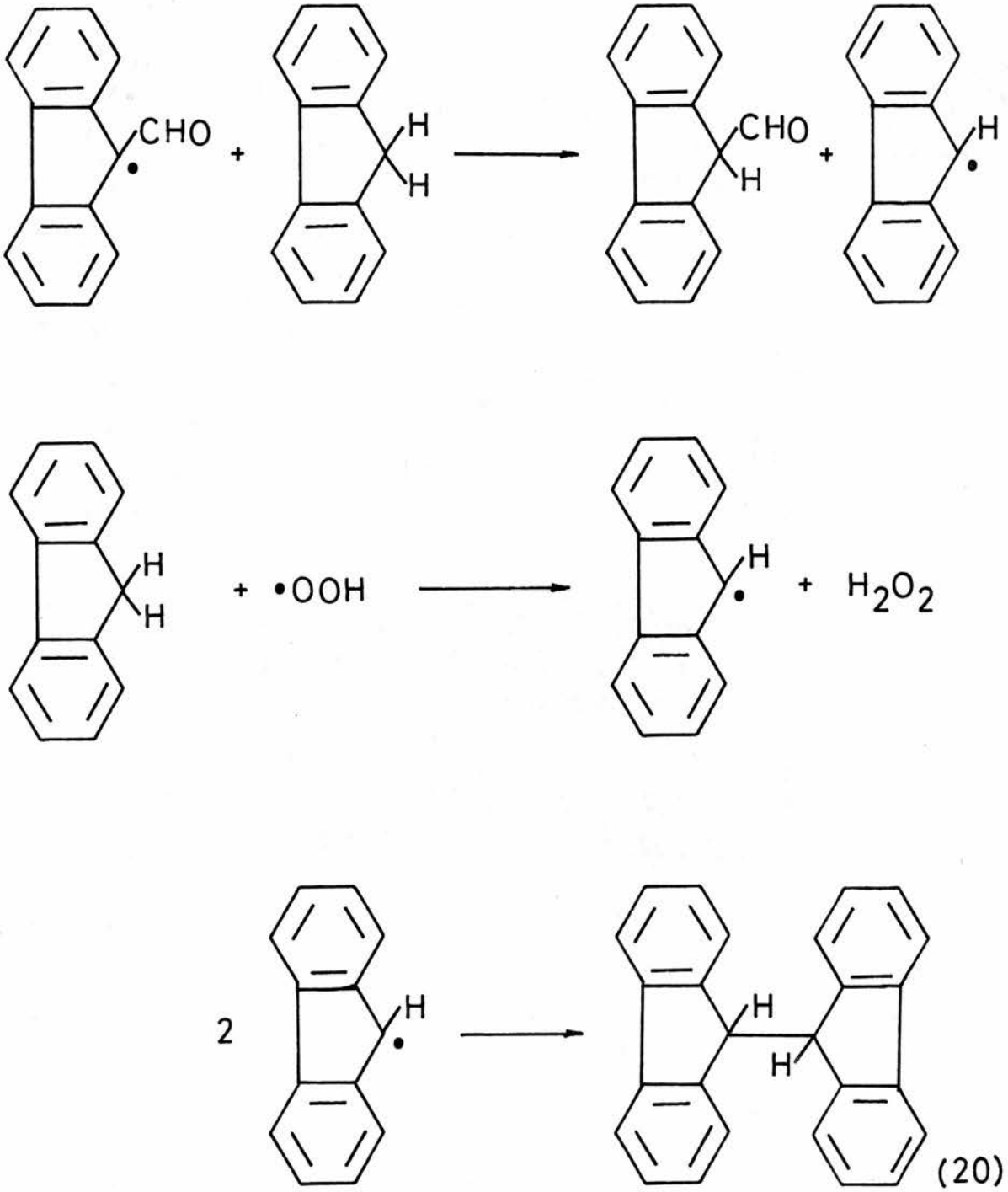


For the formation of fluorenone (21) and bifluorenyl (20) a very tentative mechanism is suggested, based on possible aerial oxidation to a hydroperoxide during decomposition. Such oxidations are known to take place with fluorene derivatives, (cf. β-9-phenylethylfluorene p. 134.), and some evidence for it in this case is the fact that decomposition of the hemiacetal did not take place so rapidly when kept

under nitrogen.



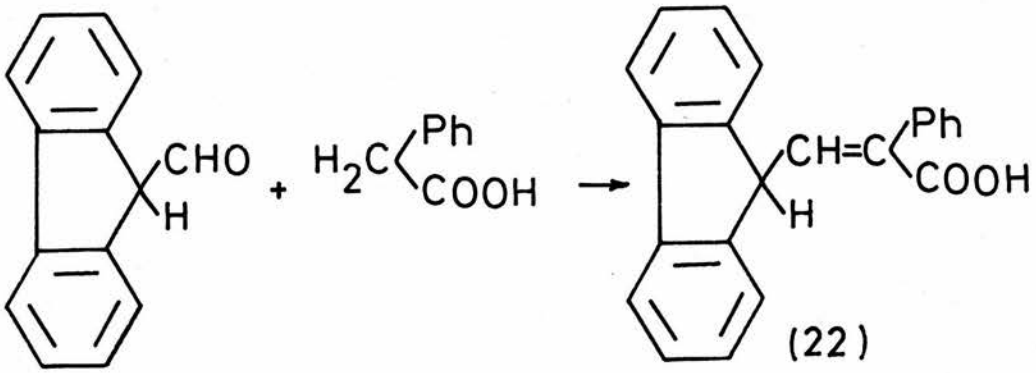
(21)

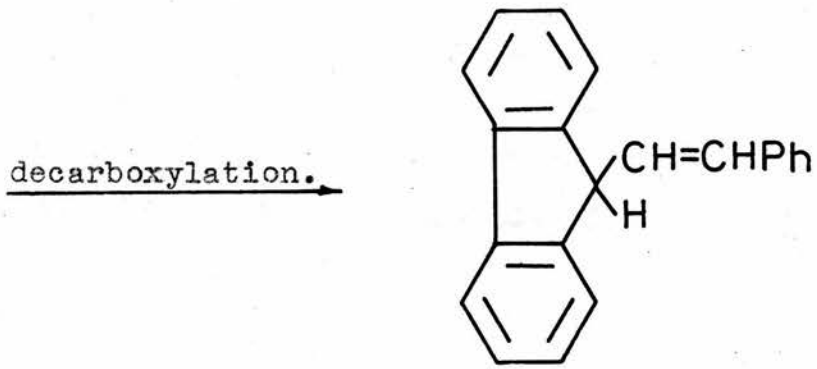


(20)

The phenylacetamide obtained from this alkaline hydrolysis resulted from hydrolysis of residual benzyl cyanide.

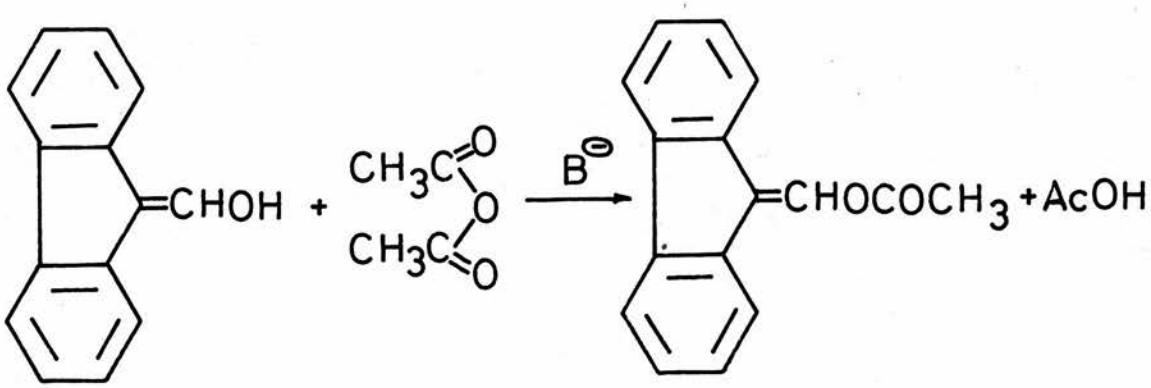
Craig's synthetic scheme having failed to produce β-9-fluorenylstyrene, an attempt was made to synthesise α-phenyl-β-9-fluorenylacrylic acid (22) direct. Decarboxylation of 22, the expected product of a Perkin condensation between 9-formylfluorene and phenylacetic acid would give β-9-fluorenylstyrene.





This condensation was carried out in acetic anhydride, with triethylamine as the basic catalyst. The product obtained was not the expected unsaturated acid 22, but the enol-acetate of 9-formylfluorene (23), formed by condensation between 9-formylfluorene in the enol form (cf. p.15) and the solvent, acetic anhydride. The unreacted phenylacetic acid

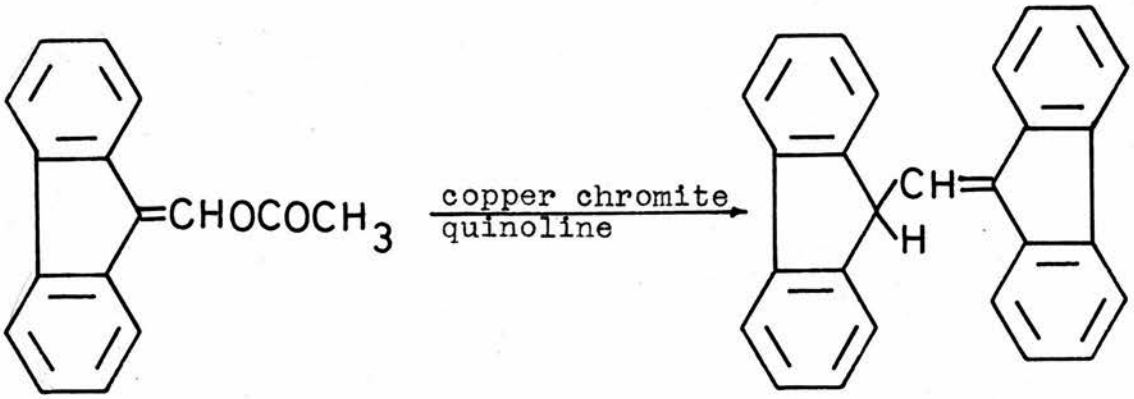
was recovered.



(23)

The compound 23 has the same melting-point as that previously reported [102], and gave no mixed melting-point depression with an authentic sample, prepared by the condensation of 9-formylfluorene and acetic anhydride in pyridine.

The enol-acetate 23, with its strong C::C and C::O absorption bands in the IR spectrum was first mistakenly regarded as the acid 22, and an attempt was made to decarboxylate it. Consequently, the enol-acetate was boiled in quinoline with copper chromite. Chromatography of the purple oil resulting from this reaction, yielded three bands. The first of these contained by far the major product, 9-fluorenyl-9-fluorenylidenemethane (24), identified by its ultraviolet and NMR spectra, and the agreement of its melting-point with that already reported[105].

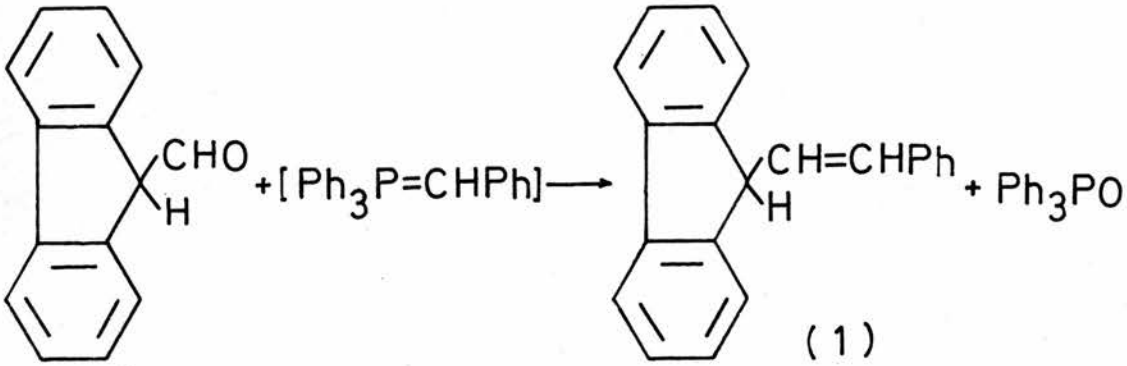


(24)

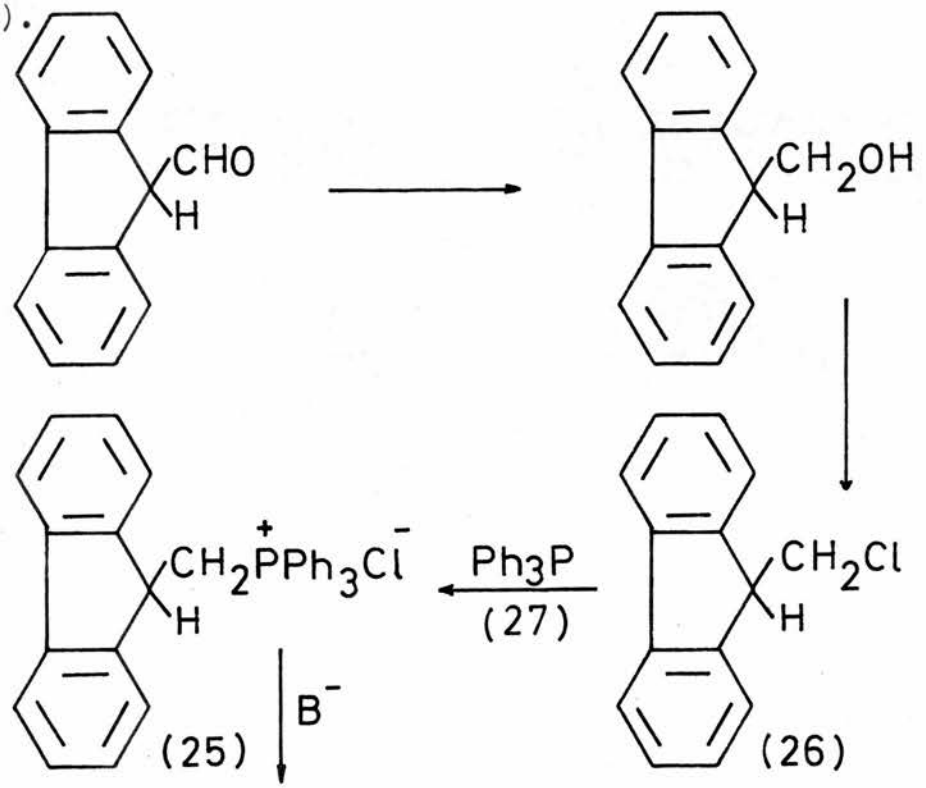
This compound, 24, was followed off the chromatography column by a buff-coloured band and then by a bright purple band. These bands gave rise to buff, and purple, coloured oils respectively, both of which on standing, very slowly produced fine yellow needles embedded in the oil. Owing to the contaminated state and small amounts of these solids, no characterisation was possible.

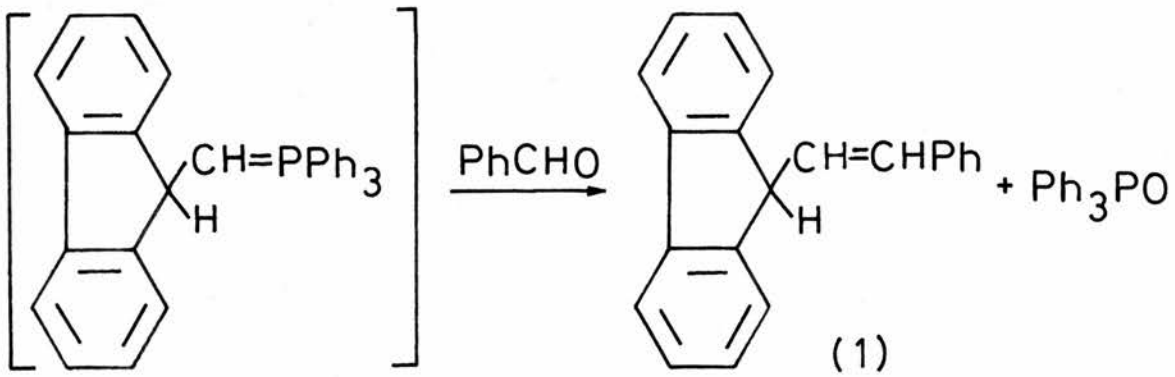
The Wittig reaction leading to olefinic products involves an intermediate phosphorane - derived from a phosphonium halide - and a carbonyl compound. This reaction offered an attractive synthetic route to β-9-fluorenylstyrene (1) as the two possible syntheses both involved the readily available 9-formylfluorene.

(a). $Ph_3P + PhCH_2Cl \longrightarrow Ph_3\overset{+}{P}CH_2PhCl^- \xrightarrow{B^-} [Ph_3P{=}CHPh]$



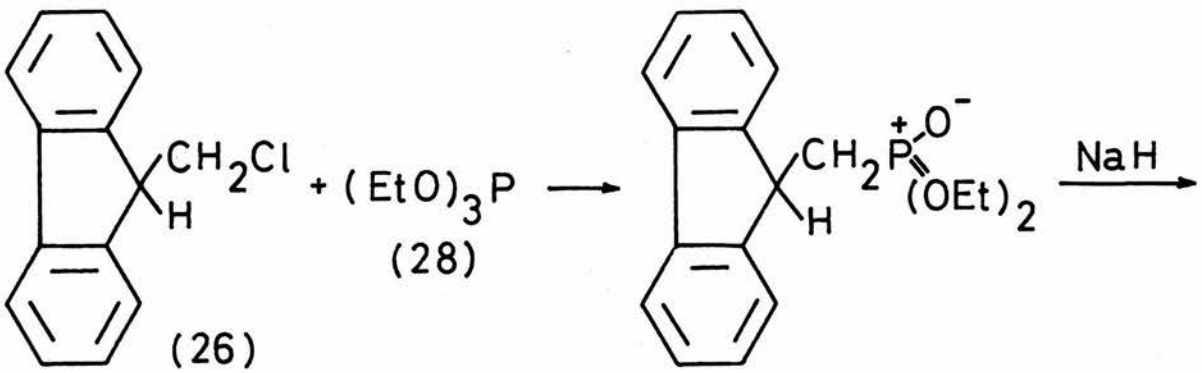
(b).

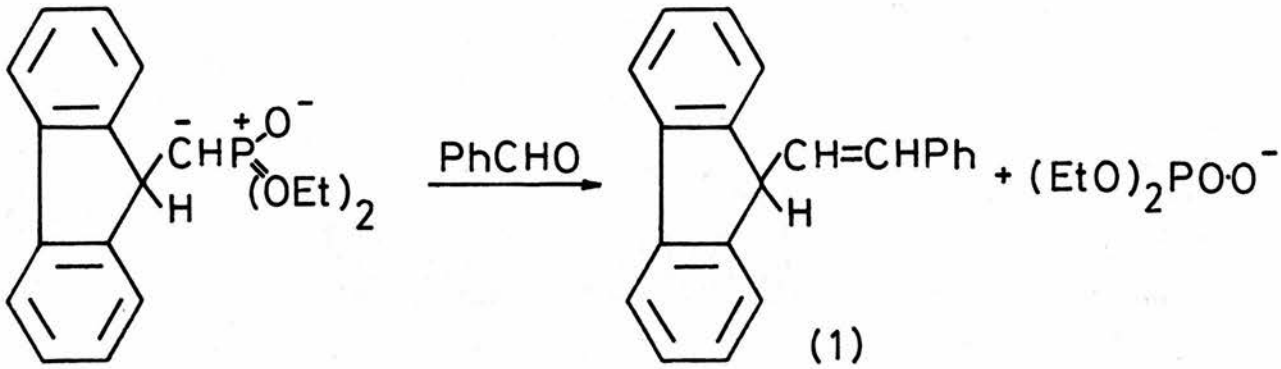




Neither of these proposed schemes, however, was successful. In the first (a), the reaction between alkali-treated benzyltriphenylphosphonium chloride and 9-formylfluorene precipitated a solid on standing. This compound, whose IR spectrum showed it to be an aldehyde, was not further identified, as, on repetition of this experiment, oils were formed, which could not be crystallised. This route was, therefore, abandoned in favour of the second scheme (b).

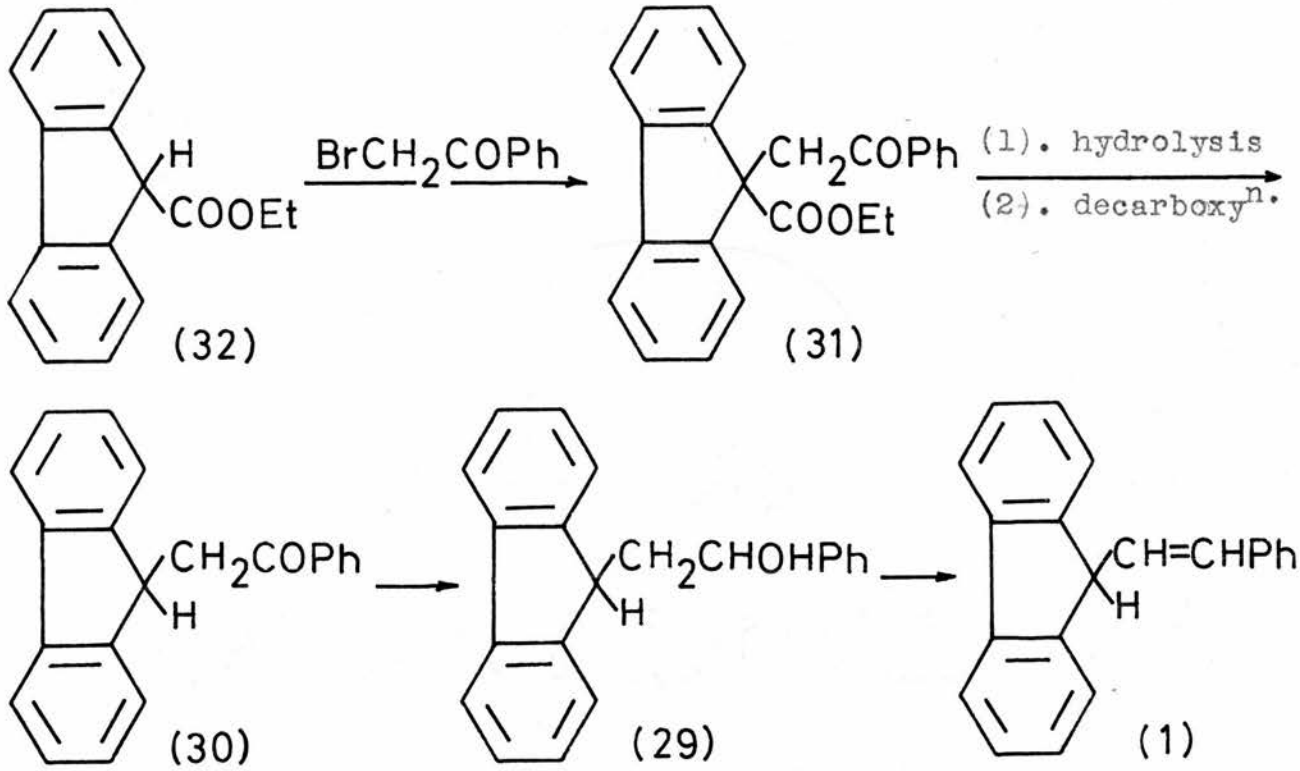
This second of the proposed Wittig reactions involved the preparation of 9-triphenylphosphoniummethylfluorene chloride (25) from 9-chloromethylfluorene (26). No reaction, however, could be induced between 9-chloromethylfluorene (26) and triphenylphosphine (27), or triethylphosphite (28), the latter compound being involved in the modified Wittig reaction [114] shown below.



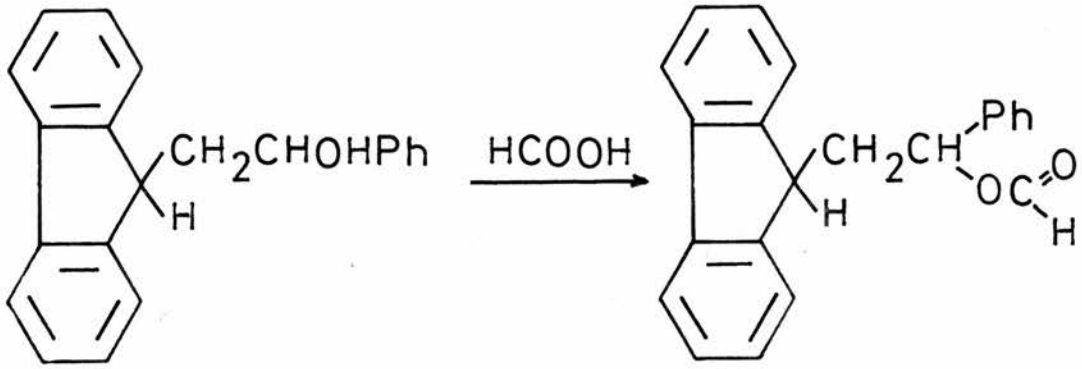


(1)

It was decided to attempt the preparation of β-9-fluorenylstyrene (1) by the dehydration of 9-(2-hydroxy-2-phenyl)ethylfluorene (29). This hydroxy compound 29, was readily prepared by sodium borohydride reduction of the corresponding ketone, 9-phenacylfluorene (30), itself easily obtained from condensation of ω-bromoacetophenone with ethyl fluorene-9-carboxylate (32) and subsequent hydrolysis and decarboxylation of the keto-ester, ethyl 9-phenacylfluorene-9-carboxylate (31).

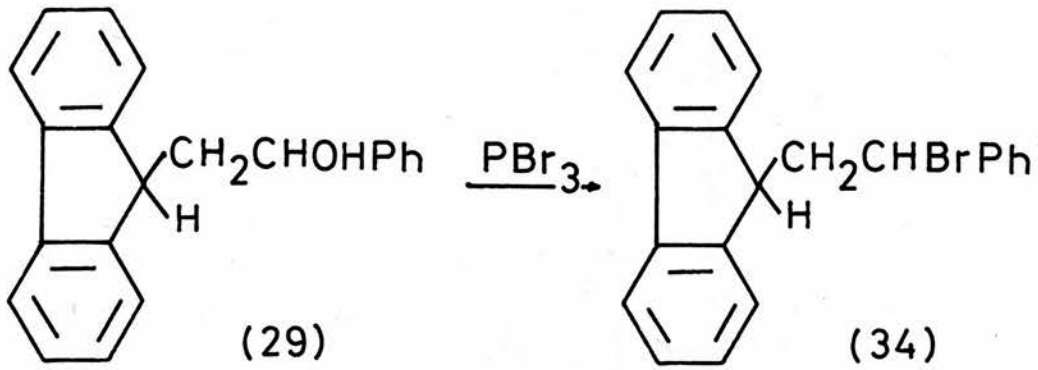


Despite repeated attempts with a variety of accepted dehydrating reagents, no olefinic compound was obtained, the only reaction product isolated being the formate intermediate 33, in the attempted dehydration with formic acid.

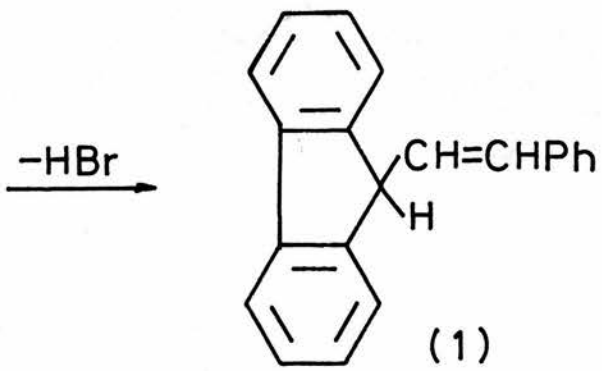


(29) (33)

Dehydration having failed, dehydrobromination of the corresponding bromide, 34, was contemplated.

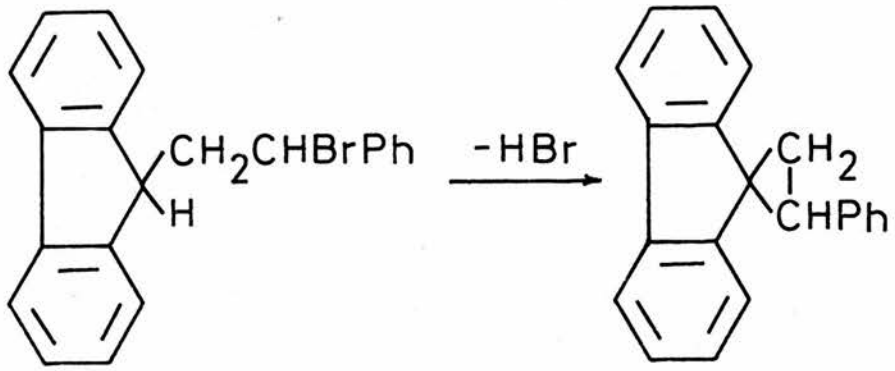


(29) (34)



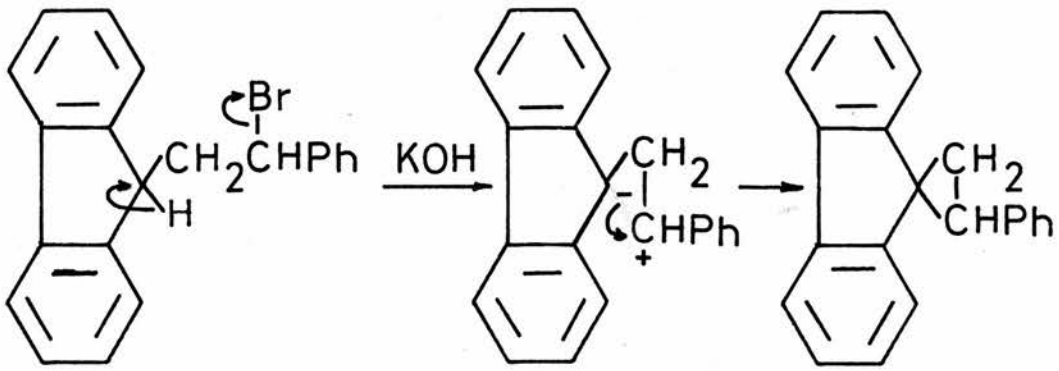
(1)

The bromide 34 was readily prepared from the alcohol 29 with phosphorus tribromide. Dehydrobromination was achieved with ethanolic potassium hydroxide, but not, however, as envisaged. Hydrogen was abstracted not from the methylene group, but from the 9-fluorene position to give spiro-1-(9-fluorenyl)-2-phenylcyclopropane (35).



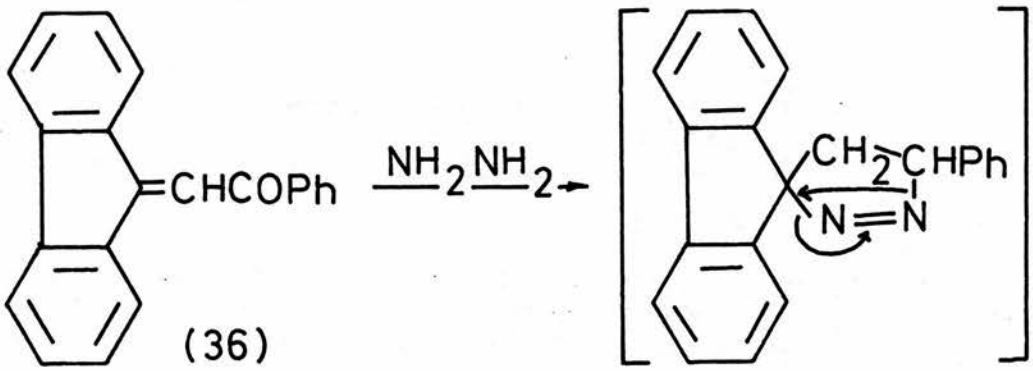
(35)

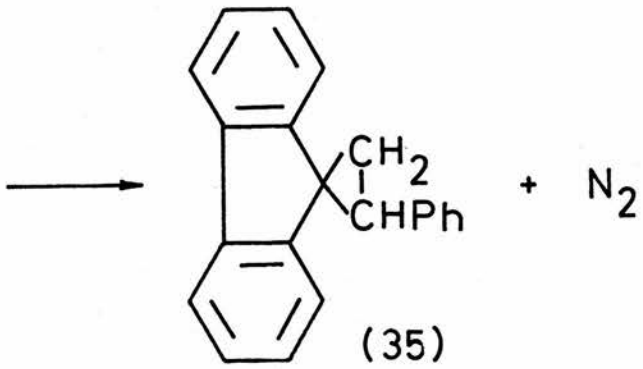
The formation of this cyclopropane derivative in preference to the desired olefine is a reflection of the greater acidity of the 9-fluorene hydrogen as compared to that of the methylene group α to the bromide. The mechanism of formation of the bromide is, thus, readily understood.



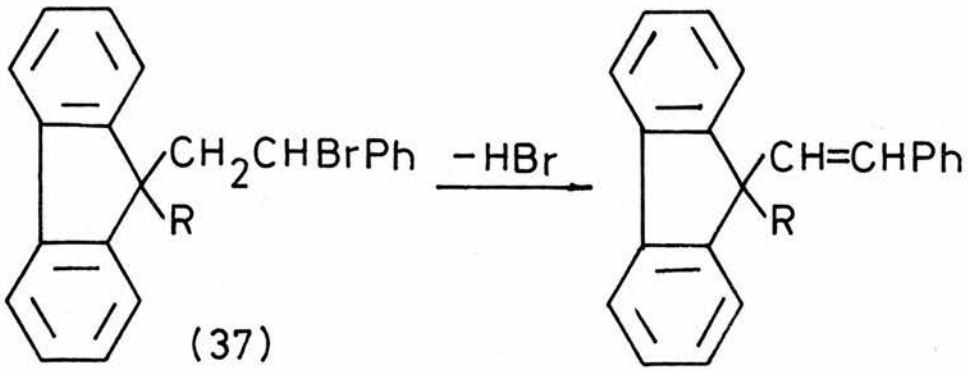
(35)

Cyclopropane derivatives can be prepared by Wolff-Kishner reduction of αβ-unsaturated ketones, the reaction proceeding through an intermediate pyrazoline [115]. Huang-Minlon modification [116] of the Wolff-Kishner reduction on 9-phenacylidenefluorene (36) [127] accordingly gave the spirocyclopropane derivative 35, obtained above.

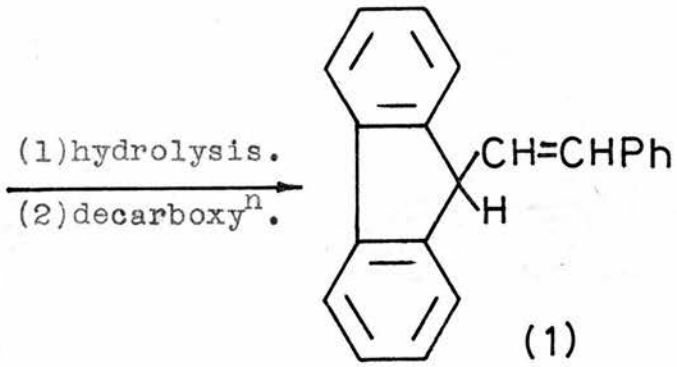




In an effort to prevent this cyclopropane formation, the same dehydrobromination reaction was contemplated with the free 9-fluorene position blocked by either a carboxylate or cyano group, which could subsequently be removed by hydrolysis and decarboxylation.

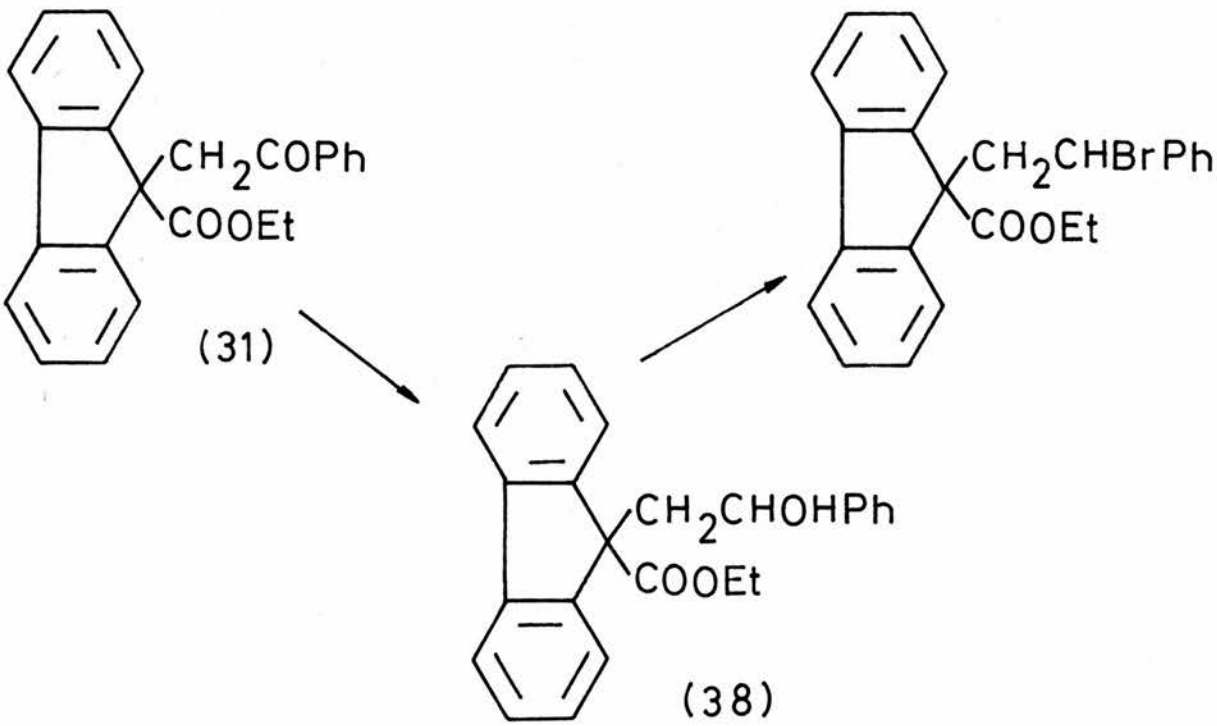


(37)



(1)

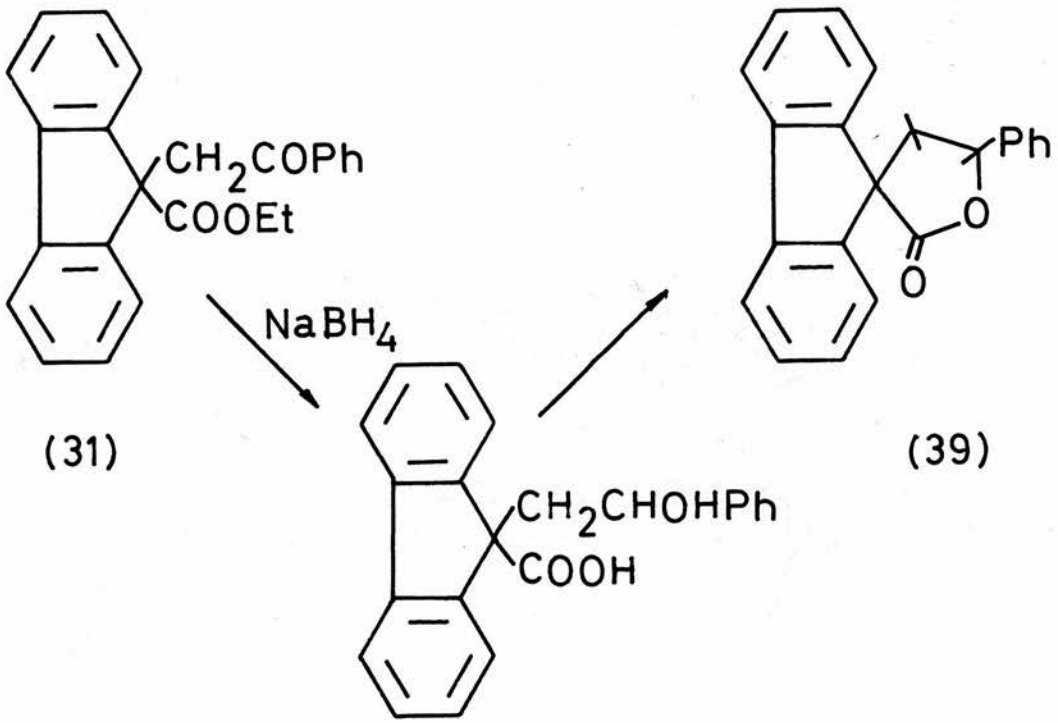
The first of these methods (37. R=COOEt) involved the following initial steps.



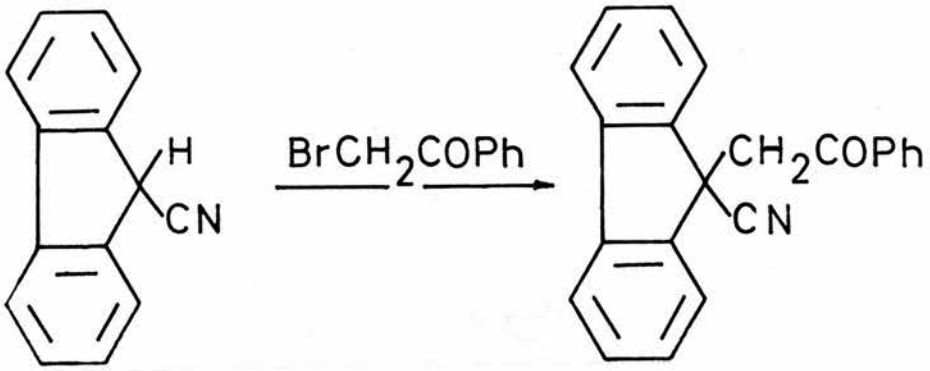
(31)

(38)

Sodium borohydride reduction of the keto-ester 31 did not give the desired hydroxy-ester 38, but spiro-1-(9-fluorenyl)-3-phenyl- λ -butyrolactone (39). Hydrolysis of the ester must have occurred along with reduction to give the λ-hydroxy-acid 40, which dehydrated to the λ-lactone 39.



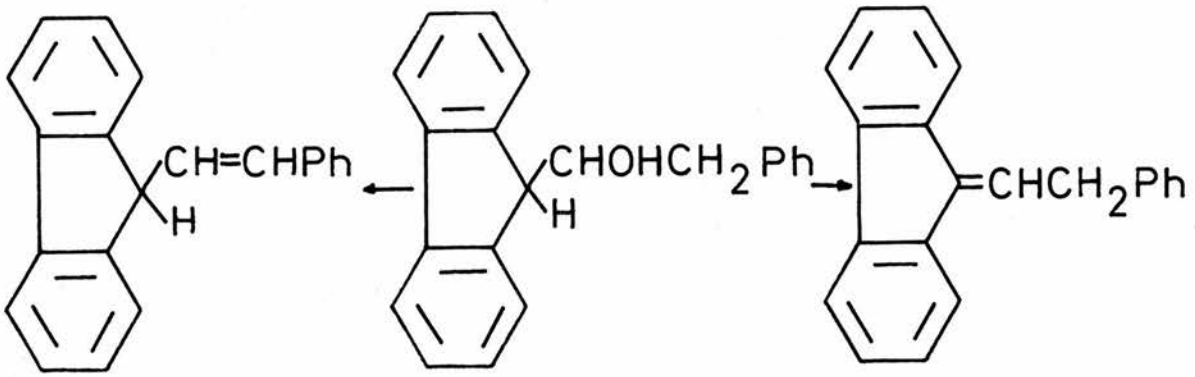
This complication would not, however, arise with the second anticipated blocking group (37. R=CN). Condensation between 9-cyanofluorene (41) [38] and phenacylbromide gave 9-cyano-9-phenacylfluorene (42).



(41) (42)

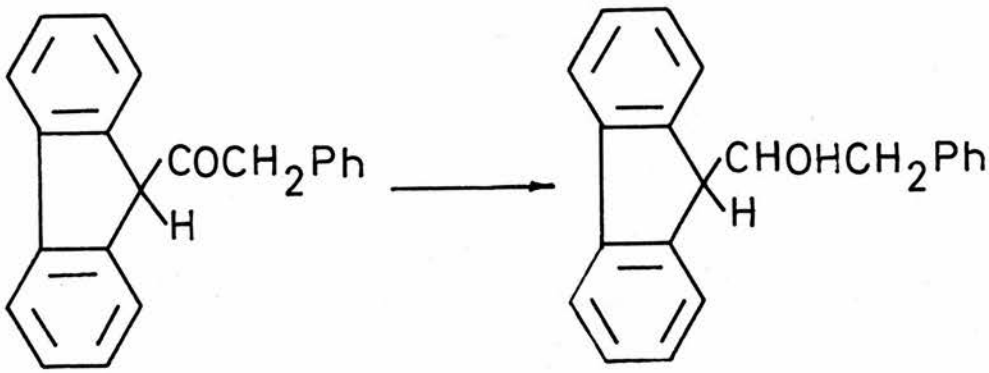
The necessary reduction of the keto-group to the corresponding carbinol could not be accomplished, and at this stage the synthesis was abandoned.

Dehydration of the isomeric 9-(1-hydroxy-2-phenyl)-ethylfluorene (43) could result in formation of 9- β -phenyl-ethylidenefluorene (2) and/or β-9-fluorenylstyrene (1).



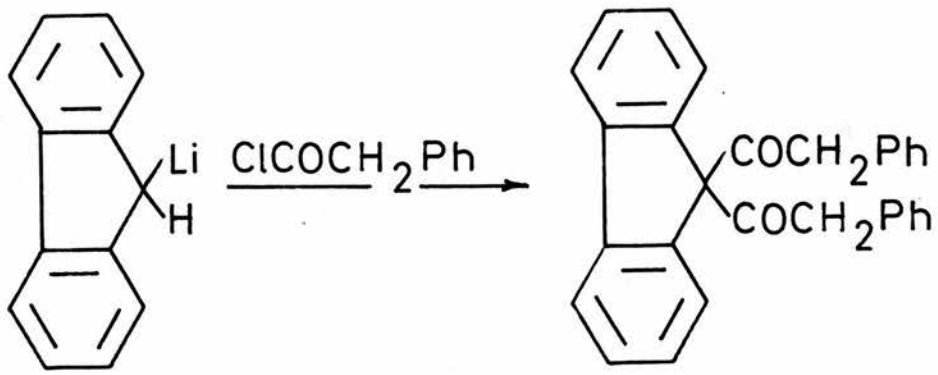
(1) (43) (2)

As with the isomer 29, preparation of 43 was envisaged from reduction of the corresponding ketone, 9-phenylacetylfluorene (44).



(44) (43)

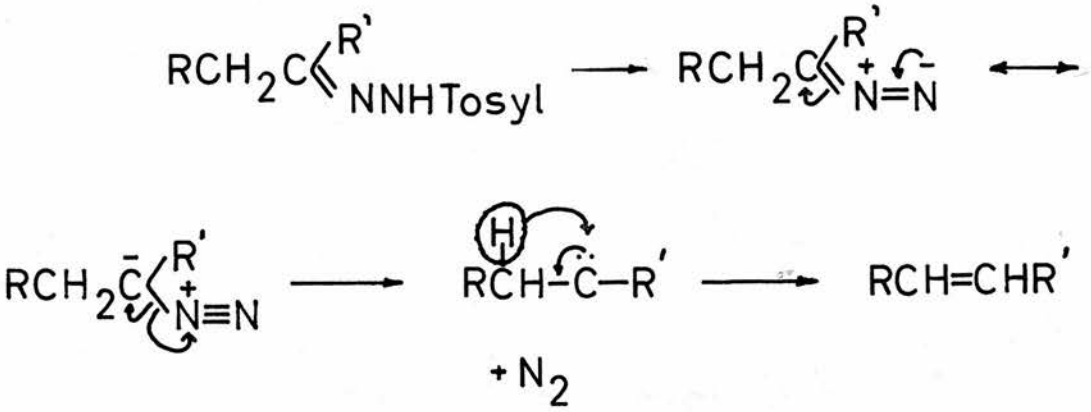
The preparation of 44 was attempted by the condensation of 9-lithiumfluorene and phenylacetyl chloride. This reaction, however, gave 9:9-diphenylacetylfluorene (45).



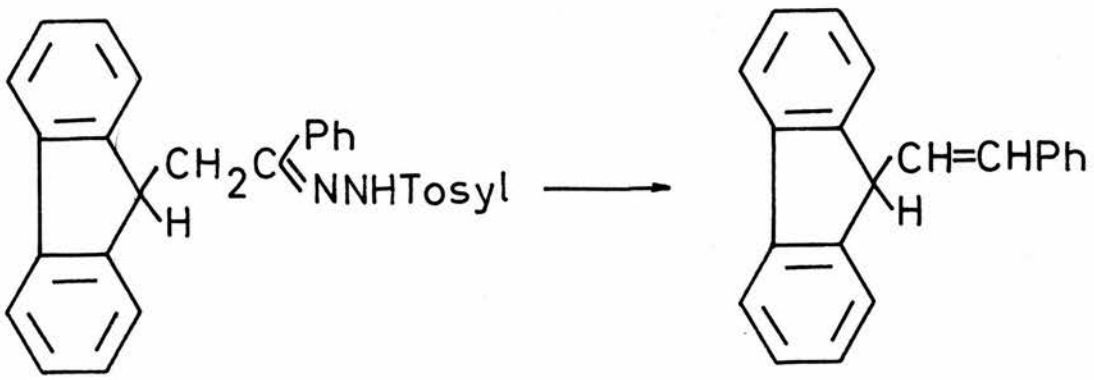
(45)

Olefinic compounds can be prepared by the alkaline decomposition of the appropriate p-toluenesulphonylhydrazone [117].

The proposed mechanism is one of proton abstraction and decomposition to give a diazo-intermediate. Further decomposition to a carbene, followed by 1:2-hydride shift, affords the olefine.



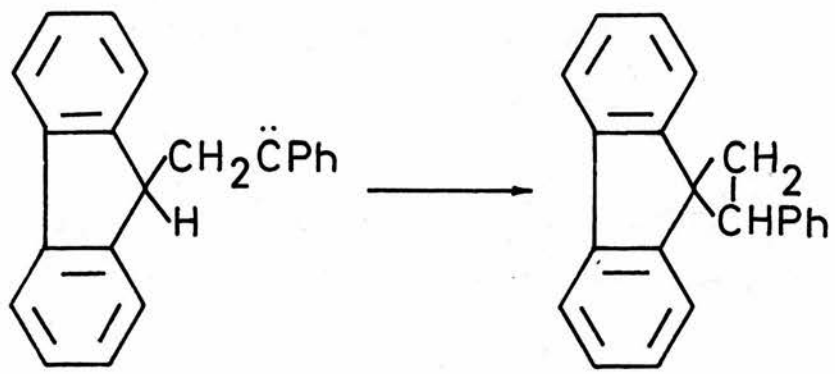
In accordance with this scheme the product from 9-phenacyl-fluorenetosylhydrazone (46) would be β-9-fluorenylstyrene (1).



(46) (1)

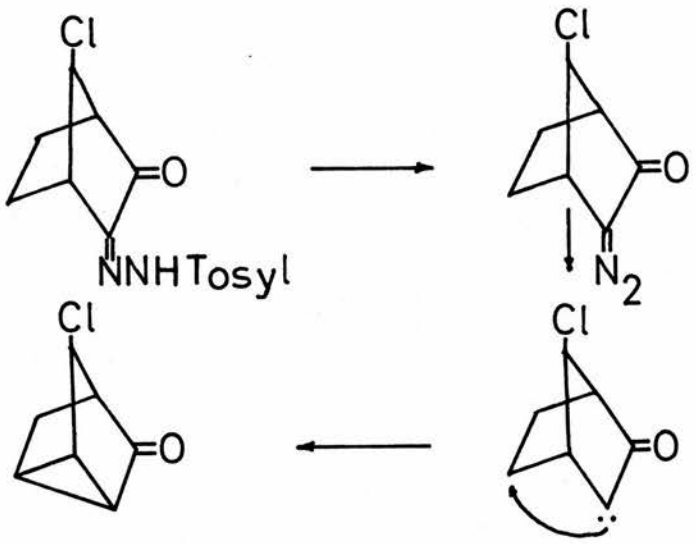
9-Phenacylfluorene (30) and p-toluenesulphonylhydrazide condensed to give 46, which, was treated with alkali. The decomposition product was not β-9-fluorenylstyrene, but spiro-1-(9-fluorenyl)-2-phenylcyclopropane (35) and 9-phenacylfluorene azine (47).

The formation of these products illustrates that the carbene intermediate 48 did not undergo the necessary 1:2-shift to produce the olefine, but underwent a carbene insertion reaction into the fluorene-C_9-hydrogen bond, to produce the cyclopropane derivative.

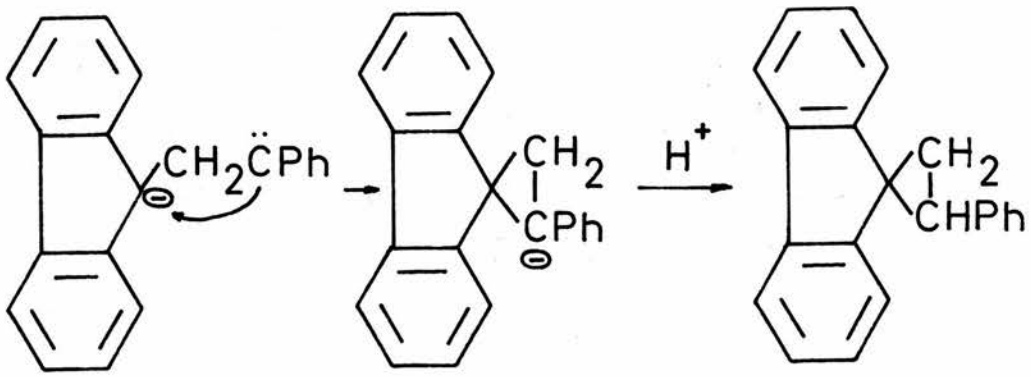


(48) (35)

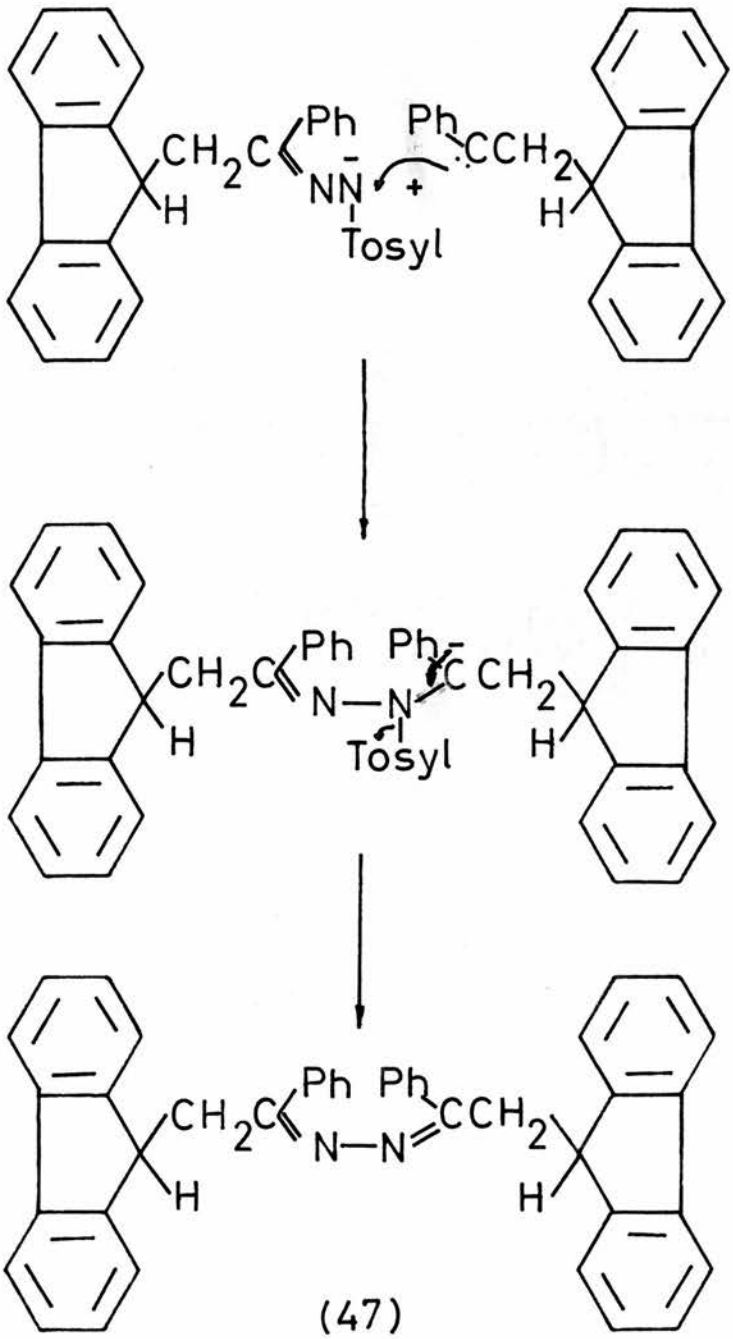
An example of a similar reaction is the cyclopropane formation from the corresponding tosylhydrazone shown below [118].



In the alkaline conditions of the decomposition, it is possible that the fluorene derivative exists as a fluorenyl anion, in which case another possible mechanism is attack by the electrophilic carbene on the 9-fluorenyl anion, followed by protonation.



Azine formation in an analogous decomposition of a tosylhydrazone has been reported [119], and adaption of the suggested mechanism to this present reaction gives the following scheme.

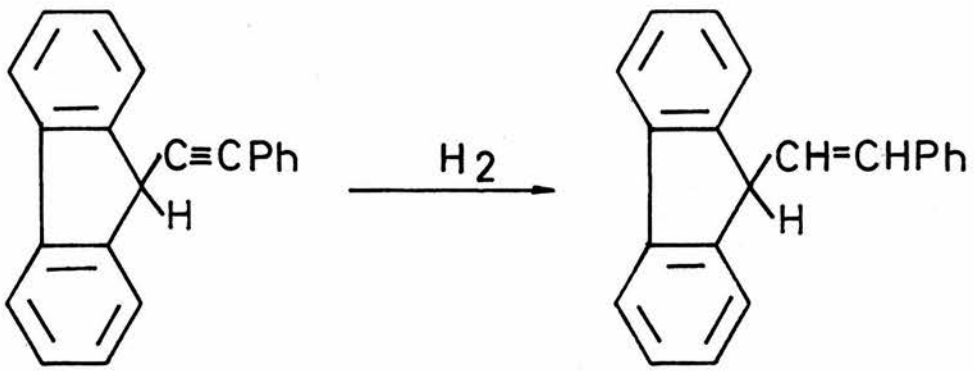


(47)

The azine 47 was also a minor product in the preparation of 9-phenacylfluorenetosylhydrazone, resulting from the condensation of two molecules of 9-phenacylfluorene with residual hydrazine hydrate, from the preparation of p-toluenesulphonylhydrazide from hydrazine hydrate and p-toluenesulphonylchloride.

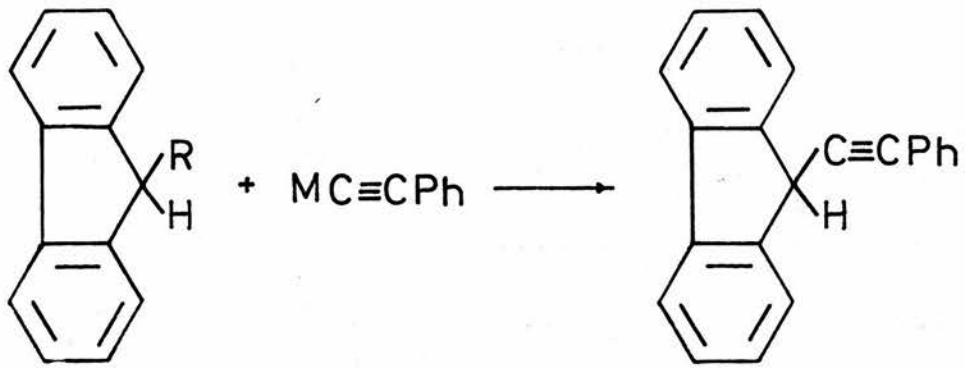
An attempt to prevent the formation of the cyclopropane derivative 35, by blocking the free 9-fluorenyl position by a cyano group failed, no condensation between 9-cyano-9-phenacylfluorene (p.122) and p-toluenesulphonylhydrazide being achieved.

Alkene derivatives can be prepared by the partial hydrogenation of the corresponding alkyne compounds. Partial reduction of 9-phenylethynylfluorene (49) would give β-9-fluorenylstyrene (1).



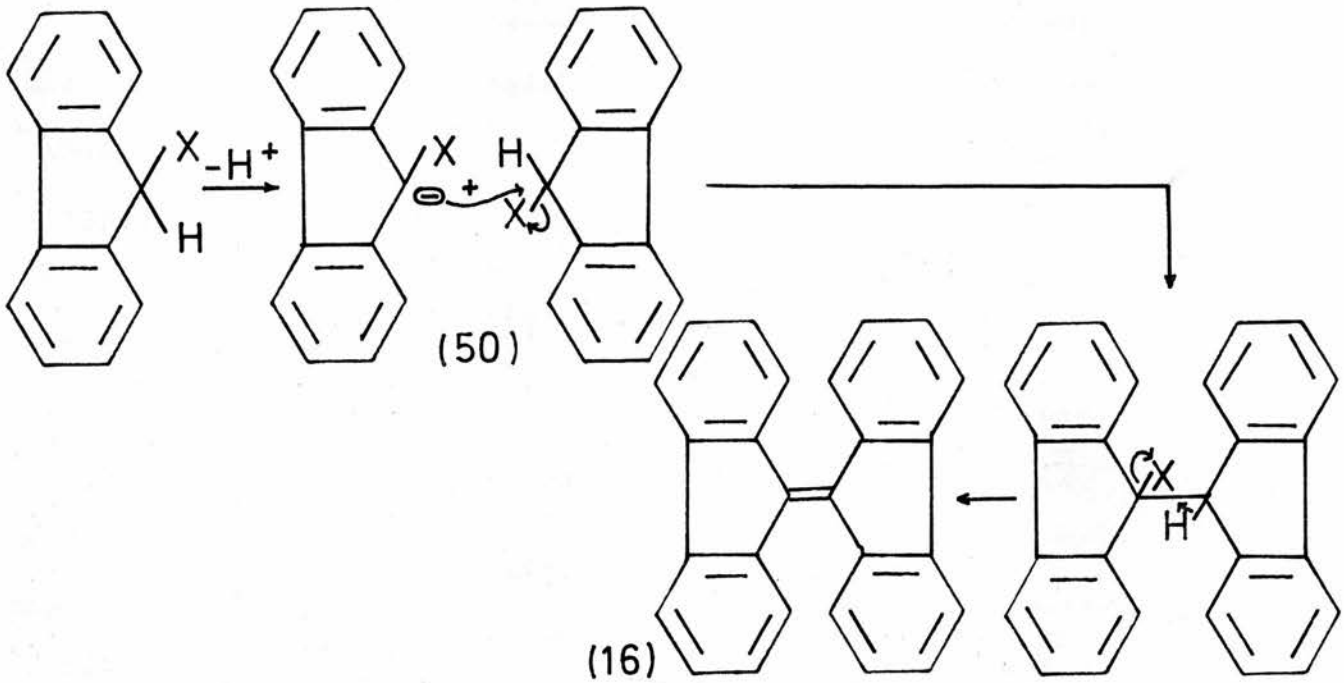
(49) (1)

9-Phenylethynylfluorene has been reported [120] as having been prepared by the condensation of 9-chlorofluorene and sodium phenylacetylene (R=Cl, M=Na), and by the condensation of fluoren-9-ol with phenylacetylene (R=OH, M=H) in concentrated sulphuric acid.

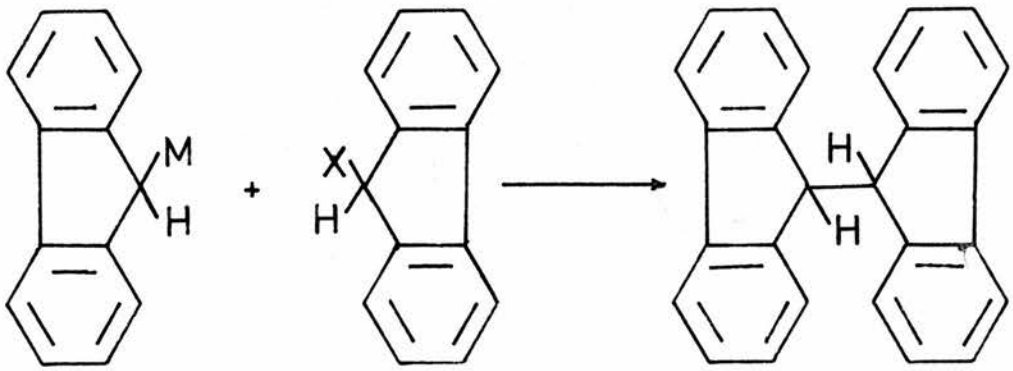


This work could not be repeated. The first method, with R=Cl and Br, and M=Na and Li, afforded, after chromatography on alumina, mainly bifluorenylidene (16), with a very little bifluorenyl (20). The second method gave unchanged fluoren-9-ol.

The formation of bifluorenylidene is readily understood by the formation in the basic medium of the 9-halofluorenyl cation (50, X=Cl or Br) which displaces halogen from another molecule of 9-halofluorene, followed by β-elimination of hydrogen halide [121].



The formation of bifluorenyl (20) can be explained in terms of residual sodium [122], or sodamide [24] used in the preparation of sodium phenylacetylene, and residual phenyllithium [122], used in the preparation of lithium phenylacetylene, leading to the formation of 9-sodio (51. M=Na) and 9-lithiofluorene (51. M=Li) respectively, which reacted with the 9-halofluorene (52. X=Br or Cl) to give bifluorenyl (20).



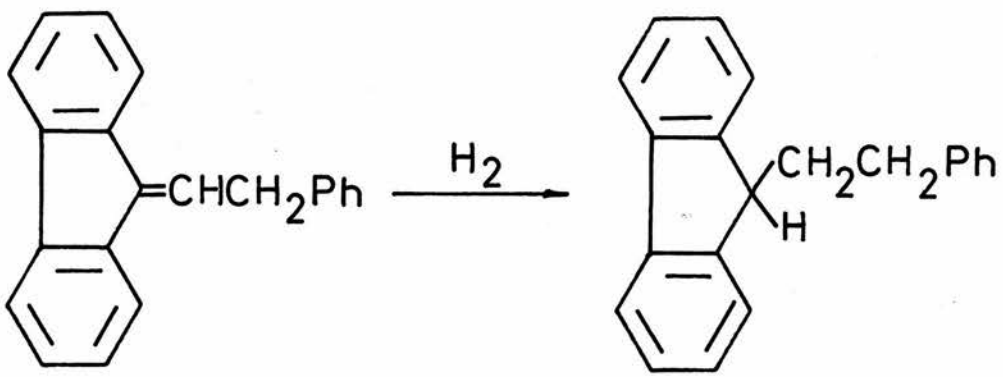
(51) (52) (20)

SECTION II - PART III

Synthesis of 9-β-Phenylethylfluorene.

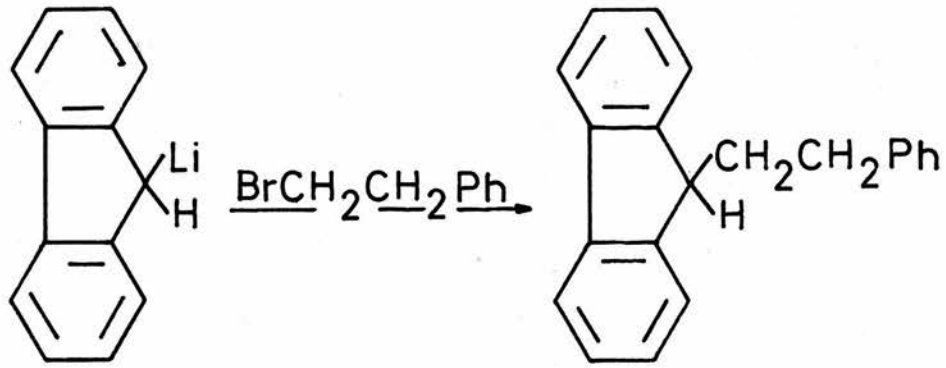
9-β-Phenylethylfluorene (3) is the saturated analogue of the isomeric compounds β-9-fluorenylstyrene (1) and 9-β-phenylethylidenefluorene (2), already mentioned in Parts I and II of this section. It has been reported [123] as having the suspiciously high melting-point of 209-10°C.

It was, therefore, decided to examine the compound, and we have synthesised it in two ways. The first was the hydrogenation of 9-β-phenylethylidenefluorene (2) with a palladium-charcoal catalyst, a platinum catalyst having failed to achieve hydrogenation.



(2) (3)

The second method was the condensation of 9-lithium-fluorene and β-phenylethyl bromide.



Although 9-sodiumfluorene had been used [24] successfully to prepare 9-methylfluorene by condensation with methyl iodide, with phenylethyl bromide this heterogeneous reaction gave bifluorenyl (20) and bifluorenylidene (16). The condensation of 9-lithiumfluorene - prepared very much more easily than its sodium counterpart - and phenylethyl bromide was a very clean, homogeneous reaction giving the desired product.

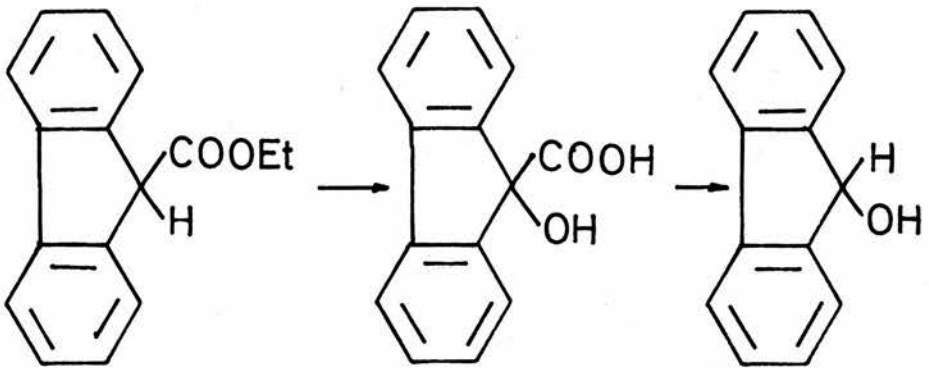
9-β-Phenylethylfluorene is a white crystalline compound, melting-point 38-39°C., which crystallised with some difficulty from ethanol. A mixed melting-point of the products of the above two preparations showed no depression. Their infrared spectrum were identical, and the ultraviolet spectra similar

to those of fluorene and 9-methylfluorene.

Unlike 9-benzylfluorene, 9-phenylethylfluorene was found to decompose over a period of weeks to an oil, the IR spectrum of which showed a strong absorption at 3450 cm^{-1}. ($OO-H_{st}$). Aerial oxidation to the hydroperoxide has most probably occurred.

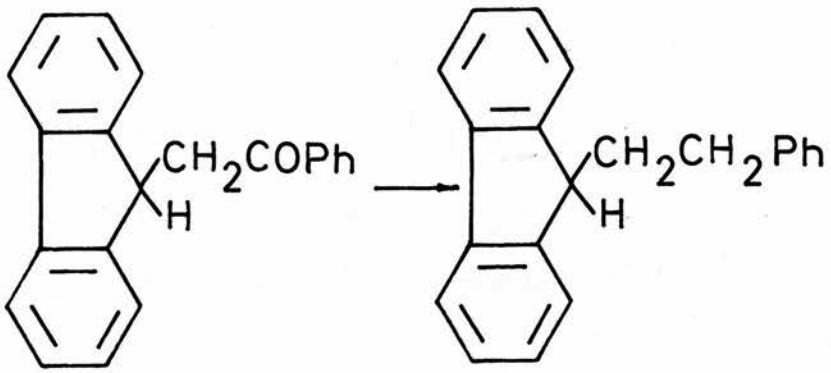
Attempted syntheses of 9-β-phenylethylfluorene.

Although the synthesis employing 9-lithiumfluorene and phenylethyl bromide was successful, a similar reaction tried previously, using ethyl 9-sodiumfluorene-9-carboxylate, formed by treatment of ethyl fluorene-9-carboxylate (32) with sodium hydride, resulted, by aerial oxidation, in the formation of fluoren-9-ol-9-carboxylic acid (53), which decarboxylated to fluoren-9-ol (54).



(32) (53) (54)

The reduction of 9-phenacylfluorene (31) would yield 9-phenylethylfluorene (3).



(31) (3)

A Clemmensen reduction with zinc-amalgam and hydrochloric acid gave only oils, which could not be crystallised.

The Huang-Minlon modification [116] of the Wolff-Kishner reduction was carried out by heating 9-phenacylfluorene, potassium hydroxide, and hydrazine hydrate in ethylene glycol at 200°C. Fluorene was found to be subliming in the condenser. This same result was obtained when the reaction was carried out under nitrogen to eliminate the possibility of aerial oxidation. No fluorene, however, was obtained when a blank experiment, omitting the hydrazine hydrate, was carried out. Such carbon-carbon fissions are known in the fluorene series, e.g., β-9-fluorenylidenepropionitrile gave fluorene on boiling with alkali [46]. Similar treatment of ethyl α-cyano-

β-(o-anisyl)- β -(9-fluorenyl)- β -phenylpropionate gave fluorene and α-cyano- β -(o-anisyl)-cinnamic acid [94].

Employing a further modification [124] of the Wolff-Kishner reduction, 9-phenacylfluorene hydrazone and dry potassium tert-butoxide were refluxed in toluene. The desired hydrocarbon was not obtained, the products being the same as those from the alkaline decomposition of 9-phenacylfluorenetosylhydrazone, namely spiro-1-(9-fluorenyl)-2-phenylcyclopropane (35), and 9-phenacylfluorene azine (47).

A third reduction of 9-phenacylfluorene with hydrogen and palladium-charcoal achieved partial reduction of the ketone, 30, to the corresponding alcohol, 9-(2-hydroxy-2-phenyl)ethylfluorene (29).

Two further reductions designed to produce 9-phenylethylfluorene were attractive , as they utilised compounds which had previously been synthesised.

Sodium borohydride reduction [68] of 9-phenacylfluorene hydrazone gave an oil which could not be crystallised.

The same result was obtained from the attempted reduction of 9-phenylethylfluoren-9-ol (6) with hydrogen iodide and phosphorus.

EXPERIMENTAL

1. Melting-points were determined on a Kofler micromelting-point apparatus with a calibrated thermometer, and fitted with a polariser.

2. Infrared spectra (IR) were recorded on a Perkin-Elmer "Infracord". In the IR data given, the wave numbers of absorption maxima are expressed in cm^{-1}, the corresponding group being in parenthesis.

3. Ultraviolet spectra (UV) were obtained on a Perkin-Elmer 137 UV spectrophotometer. In the UV data given, the wavelengths of absorption maxima are expressed in $m\mu$ ($\log_{10} \varepsilon_{max}$ in parenthesis). Spectroscopic ethanol was used as solvent unless otherwise stated.

4. Nuclear magnetic resonance spectra (NMR) were recorded on a Perkin-Elmer R 10 (60 m/c) instrument. In the NMR data given, the numbers of protons assigned to particular signals, are the integral ratios for that spectrum.

5. Alumina was of Type-H as supplied by Peter Spence and Son, Widnes. Solvents were dried with anhydrous sodium sulphate unless otherwise stated. Light-petroleum refers to that with b.p. 60-80°C., unless otherwise stated.

6. Analyses were carried out by Drs. Weiler and Strauss, Oxford; or A. H. Baird Ltd., Edinburgh.

SECTION I

β-9-Fluorenylpropyl cyanide (55).

This compound was prepared from fluorene and allyl cyanide by the method of Brunson [34].

β-9-Fluorenylbutyric acid (79).

β-9-Fluorenylpropyl cyanide (55) was hydrolysed by the method of Tucker [37] to β-9-fluorenylbutyric acid (79).

1-Methyl-3-keto-1:2:3:10b-tetrahydrofluoranthene (81).

β-9-Fluorenylbutyric acid (56.5g.) was dissolved in anhydrous hydrogen fluoride (ca. 200 ml.) in a polythene container, the experiment being carried out in the open-air.

The container was covered with a polythene sheet and left overnight, after which the cover was removed and the residual hydrogen fluoride allowed to escape into the atmosphere. Ice was added with stirring, and allowed to melt, the aqueous layer then being extracted with hot benzene. The benzene layer was extracted with hot dilute sodium hydroxide solution before being dried and evaporated to give a clean yield of the ketone, which was crystallised from ethyl acetate.

m.p. 158-160° (Lit.[37] m.p. 159-160°).

Yield: 44g. (84%).

Uncyclised acid (10g.) was recovered on acidification

of the alkaline extract.

1-Methyl-3-keto-1:2:3:10b-tetrahydrofluoranthene hydrazone (83).

The ketone 81 (23.5g.) was suspended in boiling ethanol (150ml.) and hydrazine hydrate (20ml.) added. On continued boiling, the ketone gradually dissolved, the solution being boiled for a further half-hour. On cooling, the hydrazone crystallised and was separated by filtration. Concentration of the filtrate gave additional amounts of product. Recrystallisation from ethanol gave white needles, m.p. 150-2°.

Yield: 20.5g. (83%).

Analysis: $C_{17}H_{16}N_2$ requires N: 11.3%

found N: 10.0%

IR Spectrum: 3380 cm^{-1} (w) and 3210 cm^{-1} (w) (NH_2).

1-Methyl-1:2:3:10b-tetrahydrofluoranthene (82).

The hydrazone 83 (25g.), and potassium hydroxide (14g.) were heated in diethylene glycol (200ml.) at 190-200° for 3 hours. After cooling, this mixture was acidified with concentrated hydrochloric acid, diluted with water and extracted with chloroform. The chloroform extract was washed with water and dried, evaporation giving an oil which was chromatographed.

Chromatography. A short-column was prepared of alumina (ca.250g.) in light-petroleum. The oil dissolved in the minimum amount of a 2:1 mixture of light-petroleum and benzene was introduced on to the column and eluted with the same solvent mixture, the benzene content gradually being increased. The hydrocarbon 82 was rapidly eluted off the column, evaporation of the eluate giving a colourless oil which crystallised from ethanol as colourless needles.
m.p. 89-90° (Lit.[37] m.p. 89-91°)
Yield: 20g. (90%).

1-Methyl-3-hydroxy-1:2:3:10b-tetrahydrofluoranthene (84).

The ketone 81 (2.35g.) was dissolved in the minimum amount of boiling ethanol and sodium borohydride (1g.) added. After boiling for a further half-hour, the ethanol was removed under vacuum, water added and extracted with ether. The dried ether extract was evaporated to give a colourless oil which crystallised from light-petroleum as colourless prisms.
m.p. 115-116°.
Yield: 2.3g. (95%).

Analysis: $C_{17}H_{16}O$	requires	C: 86.4%	H: 6.8%
	found	C: 84.0%	H: 7.1%

IR Spectrum: 3280 cm^{-1} (m) (OH).

3-(1-Methyl-1:2:3:10b-tetrahydro)fluoranthenyl formate (85).

The carbinol 84 (0.4g) was warmed on a boiling water-bath with formic acid (3ml. 90%), when it immediately dissolved, a yellow oil very shortly afterwards separating on the surface of the cloudy solution. After heating for 2 hours, dilution with water was followed by ether extraction, the ether extract being washed first with sodium bicarbonate solution, and then with water, before being dried and evaporated to a clear red oil. Chromatography of this oil through a short column of alumina gave a colourless oil which was crystallised from acetic acid.

m.p. 205-207°.

Yield: 0.3g. (67%).

Analysis: $C_{18}H_{16}O_2$ requires C: 81.8% H: 6.1%.

found C: 92.4% H: 6.3%.

IR Spectrum: 1700 cm^{-1} (s) (C=O)

1290 cm^{-1} (m) (C-O)

760-740 cm^{-1} (s) (aromatic C-H o.o.p. def.).

This analysis result is obviously that of a hydrocarbon, which the compound sent for analysis was not, as shown by the strong carbonyl absorption in the IR spectrum.

The unsaturated hydrocarbon which would have resulted from successful dehydration has the empirical formula

$C_{17}H_{14}$ requires C: 93.5% H: 6.5%

found C: 92.4% H: 6.3%

The formate has possibly been pyrolysed to the unsaturated compound during the drying of the sample in preparation for analysis.

1-Methyl-3-keto-1:2:3:10b-tetrahydrofluoranthene tosylhydrazone (86).

The ketone 81 (12.g.) and tosylhydrazide (0.9g.) were boiled in ethanol (15ml.), solid beginning to separate after half-an-hour. The solution was allowed to cool, and the precipitate collected by filtration. Concentration of the filtrate afforded more solid, which was combined with the first batch and crystallised from ethanol.

m.p. 240° (decomposition).

Yield: 1.2g. (58%).

Analysis: $C_{24}H_{22}N_2O_2S$ requires N: 7.0% S: 8.0%

found N: 6.5% S: 7.2%

IR Spectrum: 3250 cm^{-1} (w) (NH).

Attempted reduction with sodium borohydride.

On warming the tosylhydrazone 86 (0.2g.), and sodium borohydride (0.5g.) in dioxan (25ml.) the solution turned pink. The colour disappeared after refluxing for an hour. Removal of the dioxan, addition of water, extraction with ether, drying and evaporation gave a very small amount of a yellow, amorphous compound which melted with decomposition at ca. 260°.

1-Methylfluoranthene (56).

The tetrahydro-derivative, 82, was dehydrogenated with chloranil by the method of Tucker [37], except that the crude

material was chromatographed.

The crude reaction product was dissolved in the minimum quantity of benzene and chromatographed on a short column of alumina made up in benzene, the eluent used being benzene. Crystallisation of the pale-green oil from ethanol gave colourless needles.
m.p. 74-76° (Lit.[37] m.p. 72-75°).

1-Bromomethylfluoranthene (87).

1-Methylfluoranthene (19.6g.), N-bromosuccinimide (15g.) and benzoyl peroxide (0.2g.) were refluxed in carbon tetrachloride (120ml.), the solution becoming solid after ca. half-an-hour. Refluxing was continued for a further quarter of an hour after which the solution was allowed to cool. The solid material - a mixture of 1-bromomethyl-fluoranthene and succinimide - was separated by filtration, the succinimide being removed by washing with water. After washing with methanol to remove the water, the solid was dried before being crystallised from benzene as fine yellow needles.
m.p. 174°.
Yield: 18.7g. (70%)

Analysis: $C_{17}H_{11}Br$ requires Br: 27.1%
found Br: 27.4%

NMR Spectrum: τ 1.8 -2.7 (complex. 9 Aromatic protons).
τ 4.95 (singlet. 2-methylene protons).

Fluoranthene-1-acetonitrile (88).

On gently warming 1-bromomethylfluoranthene (5g.), and sodium cyanide (1.5g.) in dimethylsulphoxide (15ml.) on a warm water-bath, the solid immediately dissolved to give a clear, red, solution, from which, after a few minutes, solid began to separate. After warming for one hour, the solution was cooled and the solid separated by filtration.

(a) Filtrate. Water was added to the filtrate and this solution extracted with ether. The ether extract was dried and evaporated to give a buff-coloured solid. Crystallisation from ethanol gave pale brown, still impure, prisms.

m.p. 125-126°.

Yield: 2.5g. (61%).

Analysis: $C_{18}H_{11}N$ requires C: 89.6% H: 4.6% N: 5.8%

found C: 87.8% H: 4.6% N: 5.4%

IR Spectrum: 2230 cm^{-1} (w) (CN)

It should be stressed that this yield of 61% was the best ever attained. Using the same procedure described, yields were almost invariably in order of 20-30%, tarry material, very insoluble in ether, being formed on the addition of water to the filtrate.

(b) Solid. The solid was dissolved in chloroform this solution being washed with water to remove any DMSO. After drying, the chloroform solution was evaporated to give a yellow solid which crystallised from benzene in small yellow prisms.

m.p. 214-216°.

Yield: 0.5g. (14%).

Analysis: 1:2-di-1-fluoranthenylethylene (89).

$C_{34}H_{20}$	requires	C: 95.3%	H: 4.7%
	found	C: 91.4%	H: 4.8%

Due to the insolubility of this substance, an NMR could not be obtained.

Using 2-methoxyethanol as solvent.

1-Bromomethylfluoranthene (0.3g.) and sodium cyanide (0.1g.) were boiled in 2-methoxyethanol (5ml.) for 5 hours, the solution developing a red colour. After cooling, water was added and the aqueous solution extracted with a 1:1-ether:benzene mixture. Drying and evaporation gave a tarry material which, from ethanol, gave crude nitrile.
Yield: 0.1g. (40%).

Fluoranthene-1-acetic acid (90).

As purification of crude fluoranthene-1-acetonitrile resulted in considerable loss of material, the hydrolysis was carried out on the crude material.

Crude fluoranthene-1-acetonitrile (0.9g.) was boiled in a mixture of 2-methoxyethanol (5ml.) and 10N potassium hydroxide solution (7ml.) for ca. 6 hours, by which time ammonia had ceased to be evolved. After cooling and diluting with water the product was precipitated by acidifying with concentrated hydrochloric acid. The precipitated acid was extracted with ether, the ethereal extract being

thoroughly washed with water, dried and evaporated to give the acid as a crude solid, which crystallised from decalin as colourless needles.

m.p. 235-243° (decomposition).

Yield: 0.5g. (52%).

Analysis: $C_{18}H_{12}O_2$ requires C: 83.1% H: 4.7%

found C: 82.8% H: 4.5%

IR Spectrum: 1690 cm^{-1}. (s) (C=O).

Fluoranthene-1-acetyl chloride (92).

Fluoranthene-1-acetic acid (0.57g.) dissolved in thionyl chloride (5ml.) on warming to give a clear yellow solution. Removal of excess thionyl chloride under reduced pressure gave a solid which crystallised from light-petroleum (b.p. 80-100°) in almost colourless plates.

m.p. 131-133°.

Yield: 0.40g. (66%).

Analysis: $C_{18}H_{11}OCl$ requires Cl: 12.7%

found Cl: 10.9%

IR Spectrum: 1785 cm^{-1}. (s) (C=O).

2-Keto-1:2-dihydrobenzo(ghi)fluoranthene (93).

Fluoranthene-1-acetyl chloride (0.72g.) dissolved in methylene chloride (9ml.) was added dropwise to a stirred suspension of powdered aluminium chloride (0.5g.) in methylene chloride (5ml.). The solution immediately coloured and a brick-red precipitate separated out. After

stirring overnight a mixture of dilute hydrochloric acid and ice was added to this mixture, a yellow semi-solid material being formed. This was extracted with ethylene dichloride, the extract being thoroughly washed with warm dilute hydrochloric acid and then water. Washing with dilute sodium bicarbonate to remove any unreacted starting material followed by a final washing with water, drying, and evaporation gave a yellow, amorphous, solid, which melted between 170-180°.

Yield: 0.32g. (49%).

IR Spectrum: 1680 cm^{-1}. (s) (C=O).

1:2-Dihydrobenzo(ghi)fluoranthene (94).

Crude 2-keto-1:2-dihydrobenzo(ghi)fluoranthene (0.22g.) was heated with hydrazine hydrate (1ml., 98%) in diethylene glycol (5ml.) in an oil bath at ca. 80-100° for an hour. Potassium hydroxide pellets (0.2g.) were then added and the mixture heated at 180-195° for 2-3 hours, before being allowed to cool. Dilution with water and acidification with concentrated hydrochloric acid was followed by extraction with chloroform, the chloroform extract being washed with dilute sodium bicarbonate, and water before being dried and evaporated, giving a yellow oil.

This oil was chromatographed through an alumina column made up in light-petroleum, the solid being introduced dissolved in a 2:1 mixture of benzene and light petroleum. Elution

initially was with 2:1 benzene-light petroleum mixture gradually increasing in percentage benzene. Evaporation of the fractions gave a yellow oil, which was crystallised from a benzene light-petroleum mixture as yellow prisms. m.p. 123-125°.

Yield: 0.07g. (33%).

Analysis: $C_{18}H_{12}$ requires C: 94.7% H: 5.3%

found C: 92.5% H: 5.7%

UV Spectrum:

Benzofluoranthene - 248(4.42)281(4.23)292(4.34)315.5(3.61)330.5(3.84) 350(3.82)365(3.81)

Fluoranthene - 247(4.47)284(4.20)288(4.54)312.5(3.54)327(3.90) 363(3.90)

NMR Spectrum: τ 1.8-2.8 (complex. 8 Aromatic protons).

τ 6.2-6.8 (broad peak. 4 methylene protons).

Benzo(ghi)fluoranthene (4).

1:2-dihydrobenzo(ghi)fluoranthene (0.15g.) and 2:3-dichloro-5:6-dicyanobenzoquinone (0.15g.) were refluxed in sulphur-free toluene for 3 hours during which time brown solid separated. After cooling, this solid - 1:4-dihydroxy-2:3-dichlor-5:6-dicyanobenzene (95) (0.14g.) - was separated by filtration. The filtrate was diluted with ether, washed with sodium hydroxide (5%) and then water, dried, and evaporated to give a greenish oil.

This oil was chromatographed through a small column of alumina, eluting with a 2:1 benzene:light petroleum mixture.

Evaporation of the fractions gave a greenish-yellow oil which, on leaving standing for a few days with light-petroleum (b.p. 80-100°) formed long yellow needles in the oil. It proved impossible to isolate any of these crystals for the purposes of a melting-point. To this oil-crystal mixture, dissolved in a few drops of benzene, were added a few drops of a saturated solution of picric acid in benzene, an orange precipitate immediately forming. This precipitate was filtered on a micro-filtration apparatus and recrystallised from ethanol saturated in picric acid. The melting-point of the fine orange needles obtained was 205-207°, the same as that of the dipictrate of benzo(ghi)fluoranthene viz. 205-210° obtained by the original workers [1]. Unfortunately no sample of their material was available for a mixed melting-point, nor was there sufficient of the present material for an analysis.

4-Lithio-4H-cyclopenta(def)phenanthrene (97).

This organometallic compound was prepared by the reaction between phenyl lithium and 4H-cyclopenta(def)phenanthrene. In the preparation [26] of phenyl lithium from lithium and bromobenzene it was found that the reaction did not often go to completion, lumps of lithium remaining unreacted. The modification was employed of allowing this reaction to proceed as far as possible, before filtering off and weighing the unreacted lithium. The amount of reacted lithium and hence the amount of phenyl lithium present in the solution can

readily be calculated. By measuring the volume of this ethereal solution, the concentration of phenyl lithium can be found.

To a stirred suspension of freshly-cut pieces of lithium metal (2.32g.) in sodium-dried ether (100ml.), and in an atmosphere of nitrogen, was added slowly bromobenzene (18.2ml.) in ether (25ml.) at such a rate as to ensure gentle refluxing, the mixture being heated for a further quarter-hour after addition of all the bromobenzene. When no more reaction was seen to be taking place on the surface of the lithium, the solution was filtered through a plug of cotton wool. The unreacted lithium (0.80g.) was collected and weighed, and the amount of lithium (1.52g. 0.22g. atoms) converted into phenyl lithium (0.11g. moles.) calculated.

To a stirred ethereal solution of phenyl lithium (0.11g. moles.) was added slowly an ethereal solution of 4H-cyclopenta(def)phenanthrene (0.11g. moles., 20.9g.). The solution immediately became dark red, stirring being continued for a further quarter-hour after addition of all the 4H-cyclopenta(def)phenanthrene.

4H-Cyclopenta(def)phenanthrene-4-carboxylic acid (96).

Into a series of flasks containing finely powdered solid carbon dioxide was added, all at once, just sufficient of an ethereal solution of 4-lithio-4H-cyclopenta(def)-

phenanthrene to give a thick slurry. After a thorough shaking, these preparations were left for a few hours to allow the carbon dioxide to escape slowly into the atmosphere.

Addition of water followed by acidification of the separated aqueous layer with concentrated hydrochloric acid precipitated the desired acid, which was extracted with ether. Evaporation of the dried ethereal extract gave a solid, which crystallised from ethanol as almost colourless needles - slight pink discolouration.

m.p. 251 - 252° (Lit. 253°).

Yield: 15.5g. (63%).

Methyl 4H-cyclopenta(def)phenanthrene-4-carboxylate (62).

An ethereal solution of diazomethane was added dropwise to a stirred suspension - stirred by a teflon covered bar - of 4H-cyclopenta(def)phenanthrene-4-carboxylic acid in ether. Once all the acid had dissolved, the ether - and excess diazomethane - were removed, leaving an oil which was dissolved in light-petroleum (b.p. 80-100°) and, at the first signs of cloudiness on cooling, plunged, with scratching, into a mixture of acetone and solid carbon dioxide. The ester crystallised as colourless needles.

m.p. 60 - 61° (Lit. 61-62°).

Yield: quantitative.

β-4H-cyclopenta(def)phenanthrenylbutyric acid (80).

To a solution of methyl 4H-cyclopenta(def)phenanthrene-

4-carboxylate (2.9g.) in 2-methoxyethanol (11ml.) containing dissolved potassium hydroxide pellets (0.124g.) was added freshly distilled crotononitrile (0.94ml.). This clear, pale brown, homogeneous reaction mixture was maintained at 40-45°, and after ca. 20 hours the colour had darkened. After 4 days, when the solution was again clear brown, 2-methoxyethanol (7.5 ml.) and potassium hydroxide solution (16.3ml. 10N) were added, and the solution boiled until ammonia ceased to be evolved.

The cooled solution was diluted with water, and filtered before acidification with concentrated hydrochloric acid precipitated the product. The crude acid was ether extracted, this extract being dried and evaporated to give a solid which crystallised slowly from benzene as small white prisms.

m.p. 188-189°

Yield: 2,2g. (70%)

Analysis: $C_{19}H_{16}O_2$ requires C: 82.6% H: 5.8%

found C: 82.6% H: 5.7%

IR Spectrum: 1705 cm^{-1} (s) (C=O).

5-Methyl-3-keto-3:4:5:5a-tetrahydrobenzo(ghi)fluoranthene (98).

To β-4H-cyclopenta(def)phenanthrenylbutyric acid (1.5g.) in a polythene beaker was added anhydrous hydrogen fluoride (ca. 15ml.), the beaker covered with a polythene sheet and left overnight.

The cover was then removed, and when all the hydrogen fluoride had escaped into the atmosphere, ice was added and allowed to dissolve before extracting with hot benzene. The benzene extract was washed with hot, dilute sodium hydroxide solution and water before being dried and evaporated. The solid residue crystallised from ethyl acetate as pale brown prisms.

m.p. 190-194°.

Yield: 1.1g. (76%).

Analysis: $C_{19}H_{14}O$ requires C: 88.3% H: 5.5%

found C: 89.3% H: 5.5%

IR Spectrum: 1680 cm^{-1}. (s) (C=O).

5-Methyl-3-keto-3:4:5:5a-tetrahydrobenzo(ghi)fluoranthene hydrazone (99).

3-Keto-3:4:5:5a-tetrahydrobenzo(ghi)fluoranthene (2.7g.) was boiled in ethanol (15ml.) with hydrazine hydrate (1.5ml.) for 2 hours, after which, on allowing the solution to cool, brownish needles crystallised out, which were separated by filtration. Concentration of the filtrate afforded more material, the combined yields being recrystallised from ethanol.

m.p. 188-190°

Yield: 2.6g. (94%).

Analysis: $C_{19}H_{16}N_2$ requires N: 10.3%

found N: 10.6%

IR Spectrum: no carbonyl absorption.

5-Methyl-3:4:5:5a-tetrahydrobenzo(ghi)fluoranthene (100).

5-Methyl-3-keto-3:4:5:5a-tetrahydrobenzo(ghi)fluoranthene hydrazone (2.6g.) and potassium hydroxide (1.8g.) were heated in diethylene glycol (2.6ml.) at 185-195° for 2 hours. After cooling and acidification with concentrated hydrochloric acid, water was added and the solution extracted with chloroform. The dried chloroform extract was evaporated to a dark brown oil which solidified. This solid was chromatographed through a short alumina column, eluting with a 2:1 benzene:light-petroleum solvent mixture. Concentration of the initial fractions gave an oil which crystallised from ethanol as pale yellow needles.

m.p. 145-148°.

Yield: 1.7g. (73%)

Analysis: $C_{19}H_{16}$ requires C: 93.4% H: 6.6%

found C: 93.1% H: 6.7%

5-Methylbenzo(ghi)fluoranthene (72).

5-Methyl-3:4:5:5a-tetrahydrobenzo(ghi)fluoranthene (0.12g.)5 moles.) and chloranil (0.24g. 10 moles.) were boiled in sulphur-free xylene for two hours, the diphenol crystallising out immediately on cooling. This was separated by filtration, the filtrate diluted with ether, washed with dilute sodium hydroxide and then water before being dried and evaporated to give brick-red crystals. These crystals were dissolved in a 2:1 benzene: light-petroleum solvent mixture and chromatographed through

a short column of alumina, eluting with this same solvent mixture. Evaporation of the initial fractions gave, from light-petroleum, pale yellow needles.

m.p. 200-203°

Yield: .09g. (77%).

Analysis: $C_{19}H_{12}$ requires C: 95.0% H: 5.0% M.W.240

found C: 94.8% H: 4.7% M.W.250

NMR Spectrum: τ 1.85-2.79 (complex. 9 Aromatic protons).

τ 7.18 (singlet. 3 Methyl protons).

UV Spectrum:

5-Methylbenzo(ghi)fluoranthene:

218.5(4.56)234.5(4.66)248.0(4.61)291.0(4.26)334.0(3.81)351.0(3.85)

Benzo(ghi)fluoranthene [105]:

232.0(4.94)245.0(4.80)291.0(4.55)335.0(4.09)350.0(4.24).

5-Bromomethylbenzo(ghi)fluoranthene (101).

5-Methylbenzo(ghi)fluoranthene (1.45g.), N-bromosuccinimide (1.04g.) and a catalytic quantity of benzoyl peroxide were refluxed in carbon tetrachloride (15ml.) for one hour. On cooling, the product crystallised and was separated by filtration. Washing with water to remove the succinimide followed by washing with methanol and drying, gave yellow needles.

m.p. 163-165°.

Yield: 1.9g. (95%).

Analysis: $C_{19}H_{11}Br$ requires Br: 24.5%

found Br: 25.6%

NMR Spectrum: τ 1.95-2.76 (complex. 9 Aromatic protons)

τ 5.04 (singlet. 2 Methylene protons)

UV Spectrum:

5-Bromomethylbenzo(ghi)fluoranthene:

219.0(4.45)237.0(4.65)246.5(4.57)292.0(4.17)336.0(3.79)351.0(3.80)

5-Methylbenzo(ghi)fluoranthene:

218.5(4.56)234.5(4.66)248.0(4.61)291.0(4.26)334.0(3.81)351.0(3.85)

1:2-Di-5'-benzo(ghi)fluoranthenyl ethylene (103).

Immediately on warming 5-bromomethylbenzo(ghi)fluoranthene (0.11g., 0.3 m.moles) and sodium cyanide (0.016g.,0.3 m.moles.) in DMSO (1ml.) a clear red solution formed from which a yellow solid soon began separating. After warming for an hour, the solution was cooled and this solid filtered off. (The filtrate gave no trace of nitrile). The solid was dissolved in chloroform, washed with water, dried and evaporated to give, from benzene, short, fine, yellow prisms.

m.p. 269-271°.

Yield: 0.05g. (60%).

Analysis: $C_{38}H_{20}$ requires C: 95.8% H: 4.2% M.W.477

found C: 93.2% H: 4.2% M.W.552

Benzo(ghi)fluoranthene-5-aldehyde (104).

On warming 5-bromomethylbenzo(ghi)fluoranthene (0.11g.,

0.3 m.moles) and copper cyanide (0.03g., 0.3 m.moles) in DMSO (1.5ml.) for two hours on a water bath, a clear red-brown solution was obtained. Addition of water precipitated a yellow solid which was extracted with ethylene dichloride. This extract was washed with water, dried, and evaporated to give a yellow solid, which crystallised from ethanol as short yellow needles. A solution of this compound in dioxan restored the colour to Schiff's reagent.

m.p. 210-212°.

Yield: 0.06g. (68%).

Analysis: $C_{19}H_{10}O$ requires C: 89.7% H: 4.0%

found C: 89.0% H: 4.1%

IR Spectrum: 1695 cm^{-1}. (s) (C=O).

Benzo(ghi)fluoranthene-5-acrylic acid (105).

Benzo(ghi)fluoranthene-5-aldehyde (0.115g.) and malonic acid (0.047g.) were boiled in anhydrous pyridine for four hours on a water bath [104]. Dilute sodium bicarbonate solution and ether were added, and the alkaline layer separated. Acidification with glacial acetic acid followed by ether extraction, drying and evaporation of the ether extract, gave, from toluene, pale yellow needles.

m.p. 283-285°.

Yield: 0.06g. (58%).

Analysis: (The sample sent for analysis was not pure).

$C_{21}H_{12}O_2$ requires C: 85.1% H: 4.1%

found C: 82.1% H: 2.4%

IR Spectrum: 1695 cm^{-1}. (s) (C=O).

SECTION II - PART I

9-Phenylethylfluorene-9-ol (6).

A solution of phenylethyl bromide (11.1g., 0.06 moles) in dry ether (65ml.) was added with stirring to dried magnesium turnings (1.5g., 0.06 atoms) in dry ether (15ml.) at such a rate as to maintain gentle boiling, the reaction having been initiated by warming. To this Grignard reagent was added dropwise a solution of 9-fluorenone (3.6g., 0.02 moles) dissolved in the minimum amount of cold 50-50 benzene-ether mixture. This mixture was boiled for 7 hours with stirring. After cooling, the solution was poured on to an ice-ammonium chloride mixture, stirring until the ice had melted. After addition of benzene (50ml.), the organic and aqueous layers were separated; the former subsequently being steam-distilled to remove any phenylethyl bromide or phenylethyl alcohol. The resultant oil was extracted with a benzene-ether mixture, which, on drying and evaporation, gave a reddish oil. Crystallisation from benzene:light-petroleum gave white plates, m.p. 152-154°. A mixed melting-point with an authentic sample of fluoren-9-ol showed no depression. The filtrate, after removal of the solvent, was chromatographed through an alumina column.

Chromatography. The column was made up in benzene, (40g., alumina to 1g. of oil), and the eluent was 10% ether-benzene increasing the ether concentration by 5% every 50ml., until elution with pure ether was achieved. A pale yellow band

closely followed by a light-brown band were collected, two products being obtained.

1. 9-Phenylethylfluoren-9-ol. Recrystallised from light-petroleum as white prisms.

m.p. 59-60°.

Yield: 3.7g. (70%).

Analysis: $C_{21}H_{18}O$ requires C: 88.1% H: 6.3%

found C: 87.7% H: 6.9%

IR Spectrum: 3310 cm^{-1}. (s) (OH).

UV Spectrum:

Fluorene	262(4.25)300(4.00)
9-Methylfluoren-9-ol	274(4.10)303(4.32)
9-Benzylfluoren-9-ol	228(4.37)236(4.24)276(4.07)307(3.51)
β-(9-Hydroxyfluorenyl)-propionitrile	228(4.35)236(4.25)274(4.12)307(3.51)
9-β-Phenylethylfluoren-9-ol	228(4.37)236(4.27)276(4.09)307(3.54)
Fluoren-9-ol	228(4.38)234(4.29)271(4.14)307(3.35)

2. Fluoren-9-ol Total yield 1g. (30%).

9- β -Phenylethylidenefluorene (2).

On heating a mixture of 9-phenylethylfluoren-9-ol (4.5g.) in formic acid (90ml., 90%) on a boiling water bath, the mixture immediately became cloudy and an oil separated on the surface. After 2 hours, water was added, the aqueous solution ether extracted, and the formic acid removed by washing with sodium bicarbonate solution. The ether extract on drying and

evaporation gave an oil which solidified. Crystallisation from light-petroleum gave white needles.

m.p. 88-90°.

Yield: 4.g. (95%).

Analysis: $C_{21}H_{16}$ requires C: 94.0% H: 5.9%

found C: 94.0% H: 5.8%

IR Spectrum: 1640 cm^{-1}. (m) (C=C).

NMR Spectrum: τ 5.88 (doublet. 2 Methylene protons).

τ 3.25 (triplet. 1 Olefinic proton).

UV Spectrum:

9-Phenylethylidene-fluorene	230(4.64)247.5(4.51)257(4.66) 283(4.21)299.0(4.11)313(4.12)
9-Ethylidenefluorene	230(4.61)246.0(4.46)255(4.60) 280(4.03)297.0(4.03)311(4.00)
Fluorenylideneacetic acid	228(4.60)250.0(4.46)258(4.46) 288(4.12)302.0(4.13)315(4.12)
β-Fluorenylidene-propionic acid	230(4.66)246.0(4.59)257(4.61) 280(4.23)300.0(4.10)314(4.09)

5-Methyl-O-(9-(2-hydroxy-2-phenyl)ethylfluorene)-dithiocarbonate (Xanthate).

To a stirred solution of 9-2-(1-hydroxyl-1-phenyl)-ethylfluorene (1.5g., 5 m.moles) in anhydrous ether (20ml.) was added slowly sodium hydride (0.12g., 5 m.moles) as an oil suspension (0.24g., 50%). This solution was refluxed for 3 hours during which time it became pale brown and cloudy. Carbon bisulphide (0.38g., 5 m.moles) was added and refluxing continued for a further 3 hours, while a heavy white precipitate formed.

Addition of methyl iodide (0.71g., 5 m.moles) was followed by a further 3 hours refluxing. A white precipitate still persisted, but dissolved on the addition of water. The Ether extraction, separation of the ethereal and aqueous layers, washing, drying and evaporation of the ethereal layer gave an oil which solidified, crystallising via an oil, from light-petroleum.

m.p. 88-90°.

Yield: 1.3g. (66%).

Analysis: $C_{23}H_{20}OS_2$ requires S: 17.0%

found S: 11.4%

IR Spectrum: 1060 cm^{-1}. (s) (C=S).

1210 cm^{-1}. (s) (C-O).

β-9-Fluorenylstyrene (1).

The crude xanthate (2.7g.) was heated in an oil bath. The molten xanthate began visibly to decompose at 110°. After 10 minutes, decomposition had ceased, and the temperature had risen to 160°.

On cooling, the oil solidified, crystallisation from ethanol giving white needles.

m.p. 106-107°.

Yield: 1.8g. (93%).

Analysis: $C_{21}H_{16}$ requires C: 94.0% H: 6.0%

found C: 94.1% H: 5.9%

IR Spectrum: 980 cm^{-1}. (trans-olefinic CH o.o.p. def.)

UV Spectrum:

β-9-Fluorenylstyrene	219.5(4.38)261(4.53)293.5(3.79)303.5(3.84)
Fluorene	262(4.25)289.0(3.80)300.0(4.00)

NMR Spectrum: τ 2.25-3.00 (complex. 13 Aromatic protons).
τ 3.25 (doublet. 1 Olefinic proton).
τ 4.11 (doublet of doublets. 1 Olefinic proton).
τ 5.52 (doublet. 1 9-fluorene proton).

Ultra-violet examination of base-catalysed prototropy.

1. Sodium ethoxide as catalyst.

(a) 9-β-Phenylethylidenefluorene.

9-Phenylethylidenefluorene (5.46mg.) was dissolved in spectroscopic ethanol (25ml.). 1ml. of this solution was diluted to 25ml., including addition of 1ml. of a solution of sodium (0.1g., in 25ml., 1ml. diluted to 25ml.). The spectrum of this solution showed no detectable change for many days, the final spectrum being recorded after 12 days.

(b) β-9-Fluorenylstyrene.

β-9-Fluorenylstyrene (5.09mg.) was dissolved in spectroscopic ethanol (25ml.). 1ml. of this solution was diluted to 25ml., including 1ml. of a solution of sodium (0.12g.) in ethanol (25ml.). The spectrum of this solution taken immediately was almost identical with that of 9-phenylethylidenefluorene, showing that rapid isomerisation of β-9-fluorenylstyrene to 9-phenylethylidene-fluorene had taken place.

Attempts to isolate 9-β-phenylethylidenefluorene by this isomerisation of β-9-fluorenylstyrene were unsuccessful.

2. Potassium hydroxide as catalyst.

(a) 9-β-Phenylethylidenefluorene.

A solution of potassium hydroxide (1g.) in ethanol (15ml.) was added to a solution of 9-β-phenylethylidenefluorene (1g.) in ethanol (10ml.). With gentle warming the solution became reddish-brown, solid separating out. This solid was filtered off and fractionally crystallised from light-petroleum in which it is only sparingly soluble. A mixture of fine white needles and prisms was obtained.

m.p. 230-240°. Mixed melting-point depression with bifluorenyl.

Analysis: $C_{63}H_{48}$ requires C: 94.0% H: 6.0% M.W.804

found C: 92.9% H: 5.4% M.W.743

IR Spectrum: 760-690 cm^{-1}. (s) (aromoatic C-H o.o.p. def.).

UV Spectrum:

Cyclopenane derivative	208.5(5.20)258(4.91)300.5(4.24)306.0(4.10)
Spirofluorenylcyclopropane (35)	211.0(4.77)270(4.25)293.0(3.93)304.0(3.93)
9-β-phenylethylfluorene (3)	210.5(4.68)267(4.25)291.5(3.76)302.5(3.93)

NMR Spectrum: τ 1.9-2.9 (complex. Aromatic protons).

τ 4.85 (unassigned signal).

(b) β-9-Fluorenylstyrene.

To β-9-fluorenylstyrene (0.25g.) dissolved in warm ethanol (11ml.) was added slowly potassium hydroxide (0.5g.) in ethanol (7.5ml.). The initial yellow-brown colour slowly deepened and solid began separating even before warming, which, when commenced, produced a red solution from which more solid separated. This

was filtered and washed with light-petroleum.

m.p. 230-232°.

Yield: 0.12g. (48%).

1:1-Diphenyl-2-(9-fluorenyl)ethylene (7).

(a) This compound was prepared by the method of Schlenk and Bergmann [103]. 1-Hydroxy-1:1-diphenyl-2-(9-fluorenyl)ethane (9). was prepared as described by these same workers - a Grignard reaction with ethyl 9-fluorenylacetate and phenylmagnesium bromide. Dry hydrogen chloride gas was passed through a suspension of the carbinol (9) in a little ether, cooled in an ice water bath. Solid precipitated and was separated by filtration, dissolved in ether, and thoroughly washed with water to remove any traces of acid - sodium bicarbonate solution was not used to avoid any possible basic isomerism. Drying and evaporating the ether extract gave solid which crystallised from light-petroleum as white prisms.

m.p. 150-151°.

Analysis: $C_{27}H_{20}$ requires C: 94.2% H: 5.8%

found C: 94.1% H: 5.9%

UV Spectrum:

Compound (7).	211.5(4.75)261(4.49)291.0(3.83)302.5(3.90)
β-9-Fluorenylstyrene	219.5(4.38)261(4.53)293.5(3.79)303.5(3.84)

NMR Spectrum: τ 2.20-2.80 (complex. 18 Aromatic protons).

τ 4.17 (doublet. 1 Olefinic proton).

τ 5.28 (doublet. 1 Tertiary proton).

(b) The carbinol (9) was warmed on the water bath with formic acid (90%) for 2 hours, water added, and the aqueous solution

extracted with ether. The ether extract was washed with sodium bicarbonate solution, and water, dried, and evaporated to a solid which crystallised from light-petroleum, m.p.150-151°. No mixed melting-point depression with product from (a).

(c) The carbinol (9) was warmed on the water bath with thionyl chloride for 15 minutes, the excess thionyl chloride removed under reduced pressure, and the resultant oil crystallised from light-petroleum (slightly discoloured crystals), m.p. 150-152°. No mixed melting-point depression with product from (a).

1:1-Diphenyl-2-(9'-fluorenylidene)ethane (8).

The method used was that described by Kuhn [41]. The procedure was followed exactly, solid being obtained which melted at 113° - constant after three crystallisations, from light-petroleum.

Analysis: $C_{27}H_{20}$ requires C: 94.2% H: 5.8%

found C: 94.1% H: 5.7%

UV Spectrum:

Compound (8)	223.0(4.59)229.0(4.61)248.0(4.49)257.0(4.64) 277.0(4.20)285.5(4.23)301.5(4.16)314.0(4.18)
β-9-Phenylethylidene-fluorene (2)	230.0(4.64)248.0(4.51)257.0(4.66)274.5(4.19) 283.5(4.21)299.0(4.11)313.0(4.13)

NMR Spectrum: τ 2.10-2.90 (complex. 18 Aromatic protons).

τ 2.95 (doublet. 1 Olefinic proton).

τ 4.12 (doublet. 1 Tertiary proton).

Treatment of Compounds 7 and 8 with pyridine.

Compound 7. The hydrocarbon (7) (0.7g.) was boiled for 3 hours with anhydrous pyridine (5ml.). Ether was added and the

ethereal solution washed with dilute sulphuric acid and then water, dried, and evaporated to give a solid, which crystallised from light-petroleum.

m.p. 110-112°.

UV Spectrum: Almost identical with the spectrum of the equilibrium mixture of compounds 7 and 8. (See UV Spectrum II page 93).

NMR Spectrum: Identical with the spectrum obtained on superimposing the NMR spectra of the two isomers 7 and 8.

More careful recrystallisation from light-petroleum gave two different sets of crystals.

(i) m.p. 102-112°: impure 8.

(ii) m.p. 123-135°: impure 7.

Compound 8. Treatment of the hydrocarbon 8 (0.5g.) with anhydrous pyridine(4 ml.) as above, gave a solid m.p. 100-102°, which was shown, again by the NMR spectrum, to be a mixture of the two isomers 7 and 8.

Ultraviolet examination of base-catalysed prototropy of Compounds 7 and 8.

The spectra of the pure isomers were recorded in ethanol, and also in ethanol containing approximately 0.16g./l. of dissolved sodium metal. From a comparison of these spectra (spectra II), it is obvious that tautomerism occurs with both compounds to give a mixture, in which, 1:1-diphenyl-2-(9-fluorenylidene)ethane predominates.

Attempts to obtain an identical isomerisation product on treatment with ethanolic potassium hydroxide failed owing to solubility effects.

1:1:3-Triphenylpropene-1 (11).

This compound was prepared by the method of Koelsch and Johnson [106].

m.p. 30-32°.

1:3:3-Triphenylpropene-1 (12).

This compound was prepared by the method of Burckhalter and Johnson [107].

m.p. 94-95°.

Base-catalysed prototropy of compounds 11 and 12.

To each of these isomers (0.5g.) dissolved in ethanol (5ml.) was added a solution of potassium hydroxide (1g.) in ethanol (15ml.), the solutions being boiled for 2 hours.

After removal of the ethanol under vacuum, the residue was dissolved in ether, this extract washed with water, dried and evaporated to give oils, which, on one occasion crystallised with difficulty from ethanol, and on other occasions could not be crystallised.

The solid products from both these separate reactions melted at 40-41° and gave no mixed melting-point depression with each other.

IR Spectrum.

The IR spectra of both samples of this solid m.p. 40-41° were identical and very similar to the IR spectrum of 1:1:3-triphenylpropene-1 (11) the most noticeable difference between these spectra and the spectrum of 1:3:3-triphenylpropene-1 (12) being the absence of the strong trans-olefinic CH o.o.p. def. absorption band at 975 cm^{-1}. present in the latter. After standing for some weeks, these solids and compound 11 became oils the IR spectra of which, showed an absorption at 3450 cm^{-1}. (w) (OO-H). These oils restored the colour to starch-iodide paper.

NMR Spectra:

1:1:3-Triphenylpropene-1 (11).

τ 2.7-2.95 (complex. 15 Aromatic protons).

τ 3.78 (triplet. 1 Olefinic proton).

τ 6.58 (doublet. 2 Methylene protons).

1:3:3-Triphenylpropene-1 (12).

τ 2.55-2.95 (complex. 15 Aromatic protons).

τ 3.29 (quartet. 1 Olefinic proton).

τ 3.70 (doublet. 1 Olefinic proton).

τ 5.15 (doublet. 1 Tertiary proton).

The NMR spectra of the oils obtained from the above ethanolic potassium hydroxide treatment of both isomers were very similar to the spectrum of 1:1:3-triphenylpropene-1 (11).

SECTION II - PART II.

9-Formylfluorene (18).

Fluorene and ethyl formate were condensed by the method of Von and Wagner [36]. No purification of the initially formed product was carried out.

9-Formylfluorene methanol hemiacetal (19).

9-Formylfluorene (5g.) was boiled in ethanol (50ml.) containing dissolved sodium metal (1g.) for an hour, the ethanol then being removed from the red solution under reduced pressure. Addition of water was followed by acidification with concentrated hydrochloric acid and extraction with ether. After washing with water, the ether layer was dried and evaporated to give a red oil. This oil was dissolved in an equal volume of methanol with gentle warming. On cooling, white needles were deposited which, were recrystallised from an absolute minimum amount of methanol. These were unstable, decomposing rapidly into a yellow oil.

m.p. 55-57°.

Yield: 4.1g. (71%).

Analysis:	$C_{15}H_{14}O_2$				
		requires	C: 79.6%	H: 6.2%	OMe: 13.7%
		found	C: 78.1%	H: 6.0%	OMe: 12.9%

IR Spectrum: 3020 cm^{-1}. (m) (OH)

1135 cm^{-1}. (s) (OMe)

NMR Spectrum: (Mixture of 9-formylfluorene and hemiacetal).

τ 1.7-2.9 (complex. Aromatic region).

τ 6.58-6.70 (complex. Methoxyl of methanol and hemiacetal).

Aldehyde : τ 0.88 (doublet. Aldehydic hydrogen).

τ 5.37 (doublet. Fluorene-9-hydrogen).

Hemiacetal: τ 5.27 (doublet. Fluorene-9-hydrogen).

τ 5.90 (doublet. Hydrogen of hemiacetal group).

2:4-Dinitrophenylhydrazone: Orange-red needles m.p. 190-195°.

This same solid resulted from repetition of Craig's attempted condensation [110], of 9-formylfluorene and benzyl cyanide. The solid obtained in this case was treated with alkali as described by Craig.

Sodium hydroxide solution (17ml., 2N) was added slowly to a refluxing solution of the hemiacetal (3.5g.) in methanol (15ml.). The solution became a clear red and, after boiling for 2½ hours, the ethanol was removed, water added, and, the solution acidified with concentrated hydrochloric acid, and ether extracted. The ether extract was washed with water, dried, and evaporated to give a red oil which was chromatographed through alumina, eluting with light-petroleum benzene mixture. The following compounds were obtained from the chromatography column in the order fluorene, bifluorenyl, fluorenone and

phenylacetamide, the last named being obtained after elution with acetone. All of these compounds showed no mixed melting-point depression with authentic samples.

Yields: Fluorene - 2.1g. (84%).
Bifluorenyl - 0.08g.
Fluorenone - 0.02g.
No percentage yields are calculated for these compounds as it is felt that their respective amounts depend, not on the reaction, but on the state of the unstable hemiacetal at the start of the reaction. The amount of phenylacetamide obtained has no real significance, being purely residual.

9-Formylfluorene-enol-acetate (23).

(a) 9-Formylfluorene (15g., 0.08 g.moles), phenylacetic acid (11g., 0.08 g.moles), triethylamine (8.1g., 0.08 g.moles) and acetic anhydride (24.5g., 0.24 g.moles) were heated in a boiling water bath for 20 hours. Addition of hydrochloric acid (150ml., 10%) was followed by extraction with benzene, the benzene extract in turn being extracted with sodium hydroxide (130ml., 10%). On acidification of this alkaline extract, an almost quantitative yield of phenylacetic acid was obtained.

After washing with water and drying, evaporation of the deep-red benzene extract gave a solid which was crystallised from benzene as white needles.

m.p. 133°.

Yield: 10g. (55%).

Analysis: $C_{16}H_{12}O_2$ requires C: 81.3% H: 5.1%

found C: 81.4% H: 5.5%

IR Spectrum: 1765 cm^{-1}. (s) (C=O).

1670 cm^{-1}. (s) (C=C).

NMR Spectrum: τ 1.77 (singlet. 1 Olefinic proton).

τ 1.98-2.98 (complex. 8 Aromatic protons).

τ 7.74 (singlet. 3 Acetyl protons).

(b) 9-Formylfluorene (7.3g., 0.04 g.moles), acetic anhydride (12ml.) and pyridine (3.2ml.) were heated in a boiling water bath for 2 hours. On cooling, white needles separated.

m.p. 132-133°.

Yield: 5.5g. (62%).

9-Fluorenyl-9'-fluorenylidenemethane (24).

9-Formylfluorene-enol-acetate (3.1g.) was boiled with copper chromite (0.2g.) in quinoline (20ml.) for 45 minutes, gas seeming to be evolving. This mixture was cooled and poured into excess hydrochloric acid (50ml., 10%). Ether extraction gave, on drying and evaporation, a bright purple oil which was chromatographed through alumina. The oil, introduced on to the column in benzene and eluted with light-petroleum gave three distinct bands. The first band yielded a compound which crystallised from light-petroleum (b.p. 100-120°) in white prisms.

m.p. 203-205°.

Yield: 1.8g. (82%).

Analysis: $C_{27}H_{18}$ requires C: 94.7% H: 5.3%

found C: 93.9% H: 5.5%

UV Spectrum: 231.5(4.70)249.0(4.63)258.2(4.74)291.5(4.34) 303.5(4.36)317.5(4.28)

NMR Spectrum: τ 2.10-2.95 (complex. 16 Aromatic protons).

τ 3.50 (doublet. 1 Olefinic proton).

τ 4.16 (doublet. 9-fluorene proton).

Ethylfluorene-9-carboxylate.

Fluorene-9-carboxylic acid was prepared by condensing [59] fluorene with dimethyl oxalate, and oxidising the resultant keto-acid with hydrogen peroxide. The ester was prepared by bubbling dry hydrogen chloride gas through an ethanolic suspension of the acid.

ω-Bromoacetophenone. (phenacyl bromide).

All the phenacyl bromide used was prepared by the reaction between bromine and acetophenone in the presence of aluminium chloride [126].

Ethyl 9-phenacylfluorene-9-carboxylate (31) [125].

Ethyl fluorene-9-carboxylate (2g., 8.5 m.moles) dissolved in the minimum ethanol was added to sodium (0.2g., 8.7 m.moles) dissolved in ethanol (4ml.) followed by phenacyl bromide (1.7g., 8.5 m.moles) dissolved in the minimum ethanol. The solution which became orange, sodium bromide separating almost immediately, was refluxed for one hour, the ethanol evaporated

off, leaving an oil. This oil was washed with potassium bromide solution followed by water, before being extracted with ether. The dried ether extract on evaporation gave a clear red oil which crystallised from ethanol.

m.p. 123-124°. (Lit. 123-124°).

Yield: 2.5g. (83%).

IR Spectrum: 1720 cm^{-1}. (s) (ester C=O).
1690 cm^{-1}. (s) (aryl ketone C=O).

9-Phenacylfluorene (30).

The keto-ester (42g., 0.12 moles) dissolved in the minimum boiling ethanol was added to potassium hydroxide (13.4g., 0.24 moles) dissolved in the minimum boiling ethanol and the dark-brown mixture refluxed overnight. The ethanol was removed by distillation under reduced pressure, addition of water precipitating a crude oil which was extracted with ether. The ether extract was washed with sodium bicarbonate followed by water, dried, and evaporated to give a clear red oil. This oil, crystallised from ethanol twice, gave orange-yellow needles.

m.p. 98-99°. (Lit. 96-97°).

Yield: 30g. (89.5%).

Analysis: $C_{21}H_{16}O$ requires C: 88.7% H: 5.7%
found C: 88.6% H: 6.0%

IR Spectrum: 1690 cm^{-1}. (s) (aryl ketone C=O).

9-(2-Hydroxy-2-phenyl)ethylfluorene (29).

9-Phenacylfluorene (4g., 14 m.moles) was suspended in ethanol (20ml.) and sodium borohydride (0.5g., 130 m.moles) added. Gentle warming for half-an-hour was followed by removal of the ethanol under reduced pressure. Water was added and the white aqueous solution extracted. The dried ether extract on evaporation gave a clear, colourless oil which crystallised from light-petroleum (80-100°).

m.p. 108-110°. (Lit. 108-109° [127]).

Yield: 3.5g. (85%).

Analysis: $C_{21}H_{18}O$ requires C: 88.1% H: 6.3%

found C: 88.4% H: 6.5%

IR Spectrum: 3580 cm^{-1}. (m) (OH).

Attempted dehydrations of 9-(2-hydroxy-2-phenyl)-ethylfluorene to β-9-fluorenylstyrene.

(i) Formic acid.

The hydroxy compound (1.43g., 5 m.moles) was heated with formic acid (15ml., 90%) on a boiling water bath for 2½ hours, after which water was added and extracted with ether. The dried ether extract on evaporation gave an oil which crystallised from a benzene light-petroleum mixture as a white solid.

m.p. 104-106°. (mixed m.p. with starting material showed a depression).

Yield: 0.3g. (16%).

The compound was assigned the structure of 2-(9-fluorenyl)-1-phenylethyl-1-formate.

Analysis: $C_{22}H_{18}O_2$ requires C: 84.3% H: 5.5%

found C: 85.4% H: 6.2%

IR Spectrum: 1730 cm^{-1}. (ester C=O).

1155 cm^{-1}. (ester C-O).

Bubbling dry hydrogen chloride gas through and ethanolic solution of this formate did not succeed in completing the desired dehydrogenation.

(ii) Ethanolic hydrochloric acid.

The hydroxyl compound (0.2g.) was dissolved in ethanol (5ml.), 6 drops of concentrated hydrochloric acid added, and the solution refluxed for 2 hours. The ethanol was removed under reduced pressure, addition of water precipitating an oil which was ether extracted. The ether extract was washed with sodium bicarbonate and then water, dried, and evaporated to give an oil. This oil, which crystallised from light-petroleum was shown by mixed melting-point and identity of IR spectra to be almost a quantitative return of starting material.

(iii) Acetyl chloride.

A small amount of the hydroxy compound (0.1g.) was dissolved in acetyl chloride (4ml.) by gentle warming, and allowed to stand for one hour. On addition to a large volume of water, a white solid separated out. This was extracted with ether, washed with a little sodium bicarbonate solution,

dried, and evaporated to give an oil which could not be induced to crystallise.

(iv) Potassium bisulphite.

The hydroxy compound (0.5g.) and potassium bisulphite (0.5g.) were ground into an intimate mixture and heated at 180° for 10 minutes.

Addition of water, ether extraction, drying and evaporation afforded starting material.

9-(2-Bromo-2-phenyl)ethylfluorene (34).

9-(2-Hydroxy-2-phenylethyl)fluorene (2.86g., 0.01 mole), and phosphorus tribromide (1ml., 0.03 mole) freshly distilled under reduced pressure, were heated on the steam bath for 1½ hours. On addition of water, an oil separated and solidified. This solid was filtered off, washed with water and recrystallised from ethanol.

m.p. 114°.

Yield: 1.5g. (43%).

Analysis: $C_{21}H_{17}Br$ requires Br: 22.9%

found Br: 20.9%

Spiro-1-(9-fluorenyl)-2-phenylcyclopropane (35).

(a) To a refluxing solution of the bromide 34 (1.8g., 4.6 m.moles) in the minimum amount of boiling ethanol was added potassium hydroxide (0.28g., 4.9 m.moles) dissolved in

the minimum boiling ethanol. Immediately a transient brown colour appeared, and potassium bromide precipitated.

This mixture was refluxed for 2 hours, after which the ethanol was removed under reduced pressure, and water added. Extraction with ether, washing with water, drying, and evaporation gave a solid which was recrystallised from ethanol as fine white needles.

m.p. 130-131°.

Yield: 1.0g. (71%).

Analysis: $C_{12}H_{16}$ requires C: 94.0% H: 6.0% M.W.268

found C: 93.4% H: 6.1% M.W.243

UV Spectrum:

Spirocyclopropane (35)	211(4.77)270(4.25)293(3.93)304(3.93)
Fluorene	210(4.45)262(4.25)289(3.80)300(4.00)
9-Methylfluorene	262(4.20)289(3.65)301(3.90)

NMR Spectrum: τ 7.84 (doublet. 2 Methylene protons).

τ 6.65 (triplet. 1 Tertiary proton).

(b) Wolff-Kishner reduction of 9-phenacylidenefluorene.

9-Phenacylidenefluorene [127] (1g., 4 m.moles), potassium hydroxide (1g.,) hydrazine hydrate (1ml., 99%), and ethylene glycol (10ml.) were heated for an hour in an oil bath at 185°, and for a further hour at 195-200°. A clear oil formed on the surface of the refluxing solution. To the cooled mixture, water was added before ether extracting. The ether extract, on drying and evaporation, gave a solid which crystallised from ethanol as white needles: spiro-1-(9-fluorenyl)-2-phenylcyclopropane,

m.p. 130-131°.

A mixed melting-poimt with the product from the above dehydrobomination reaction showed no depression.

Yield: 0.8g. (85%).

Spiro-1-(9-fluorenyl)-3-phenyl- λ -butyrolactone (39).

Ethyl 9-phenacylfluorene-9-carboxylate (32) (1g.) and sodium borohydride (0.23g.) were gently warmed in ethanol (25ml.) until all the keto-ester had dissolved. After standing for 4 hours during which time a solid crystallised, water was added, the solid filtered, and recrystallised from ethanol as small white needles.

m.p. 179-181°.

Yield: 0.70g. (80%).

Analysis: $C_{22}H_{16}O_2$ requires C: 84.6% H: 5.2%

found C: 84.6% H: 5.8%

IR Spectrum: 1765 cm^{-1}. (s) (C=O).

1170 cm^{-1}. (s) (C-O).

NMR Spectrum: τ 3.98 (triplet. 1 Tertiary proton).

τ 7.05 (doublet. 2 Methylene protons).

9-Cyano-9-phenacylfluorene (42).

To a solution of sodium (0.9g., 0.04 g.atoms) in ethanol (20ml.) was added 9-cyanofluorene (7.5g., 0.04 g.moles), with sufficient ethanol to ensure its solution on warming to a dark black-green solution. On adding phenacylbromide (7.8g., 0.4 g.moles) dissolved in the minimum ethanol, the

colour became light green. This mixture was refluxed for 4 hours after which the ethanol was removed under reduced pressure. No sodium bromide separated during heating until the start of the ethanol removal. Addition of water, ether and benzene, separation of the aqueous and organic phases, drying and evaporation of the organic layer gave an oil which solidified. Crystallisation from ethanol gave clear plates.

m.p. 142-144°.

Yield: 8g. (65%).

Analysis: $C_{22}H_{15}NO$ requires C: 85.4% H: 4.9% N: 4.6%

found C: 85.1% H: 5.1% N: 4.7%

IR Spectrum: 2250 cm^{-1}. (m) (C≡N).

1680 cm^{-1}. (s) (C=O).

9:9-Diphenylacetylfluorene (45).

9-Lithiofluorene was prepared by reacting [26] fluorene and phenyl lithium, the latter compound being prepared as described in Section I Experimental page 150.

An ethereal solution of phenylacetyl chloride (3.1g.) was added dropwise to an ethereal solution of 9-lithiofluorene (3.4g.). There was an immediate exothermic reaction, the orange colour of the organo-metallic solution disappearing, and a white solid separating. After stirring for 20 minutes, water and benzene were added; the aqueous and organic layers separated; the latter washed, first with sodium bicarbonate solution, then water, dried, and evaporated. The resultant

solid crystallised from light-petroleum, in white plates.

m.p. 137°.

Yield: 5.3g. (66%).

Analysis: $C_{29}H_{22}O_2$ requires C: 86.5% H: 5.5%

found C: 86.3% H: 5.7%

IR Spectrum: 1705 cm^{-1}. (s) (C=O).

NMR Spectrum: τ 2.10-3.30 (complex. 18 Aromatic protons).

τ 6.52 (singlet. 4 Methylene protons).

UV Spectrum: 208.5(4.65)271(4.19).

9-Phenacylfluorene toluene-p-sulphonylhydrazone (46).

The toluene-p-sulphonylhydrazide used was prepared by reaction of toluene-p-sulphonylchloride with hydrazine [46].

9-Phenacylfluorene (2.8g., 0.01 moles) and toluene-p-sulphonylhydrazide (1.9g., 0.01 moles) were dissolved in the minimum boiling ethanol and refluxed for 1 hour. The mixture was allowed to cool, and the white solid which had separated during refluxing filtered off. This solid recrystallised from ethanol as white needles.

m.p. 174-176°.

Yield: 3g. (65%).

Analysis: $C_{28}H_{24}N_2SO_2$ requires N: 6.2% S: 7.1%

found N: 6.6% S: 7.1%

IR Spectrum: 3055 cm^{-1}. (m) (N-H).

1165 cm^{-1}. (s) (S=O).

On allowing the filtrate to stand, orange needles were obtained.

m.p. 190-191°.

Yield: 0.08g. (1%).

9-Phenacylfluorene azine (47).

Analysis: $C_{42}H_{32}N_2$ requires C: 87.9% H: 6.1% N: 6.0%

found C: 89.0% H: 6.0% N: 5.4%

IR Spectrum: 1565 cm^{-1}. (m) (C=N).

NMR Spectrum: τ 2.10-3.00 (complex. 26 Aromatic protons).

τ 5.34 (triplet. 2 9-Fluorene protons).

τ 6.53 (doublet. 4 Methylene protons).

Alkaline decomposition of 9-phenacylfluorene-p-toluene sulphonylhydrazone.

Note: This experiment was repeated many times and results varied as follows:-

(a) Yield of spiro-1-(9-fluorenyl)-2-phenylcyclopropane (35) alone.

(b) Yield of 9-phenacylfluorene azine (47) alone.

(c) Mixtures of 35 and 47 obtained co-crystallised.

This was thought to be perhaps a dilution effect, but no degree of control was obtained by varying the concentrations of the reactants.

(a) 9-Phenacylfluorene toluene-p-sulphonylhydrazone (0.95g., 2 m.moles) and sodium (0.05g., 2 m.moles) in ethylene glycol

(5ml.) were refluxed for 3 hours. A transient pink colour appeared at the very beginning of the reaction - formation of the diazo intermediate - and a reddish oil separated on the surface of the refluxing solution. The mixture was allowed to cool, water added, and the mixture ether extracted. The ether extract on drying and evaporation gave an oil which solidified.

Recrystallisation from ethanol and light-petroleum gave fine white needles of spiro-1-(9-fluorenyl)-2-phenylcyclopropane.
m.p. 130-131°.
Yield: 0.25g. (46%).
No mixed melting-point depression with an authentic sample.

(b) The hydrazone 46 (0.95g., 2 m.moles) sodium (0.05g., 2 m.moles) in ethylene glycol and experiment carried out exactly as in (a) yielded the orange needles of 9-phenacyl-fluorene azine, but none of the hydrocarbon.
m.p. 190-191°.
Yield: 0.32g. (58%).
No depression on mixed melting-point with azine from the preparation of the tosyl-p-hydrazone 46.

(c) Similar experiments gave, on occasion, mixtures of the white needles of the hydrocarbon and the orange needles of the azine, the hydrocarbon crystallising first.

SECTION II - PART III

9-β-Phenylethylfluorene (3).

(a) Palladium-charcoal catalyst (0.05g.) in absolute ethanol (5ml.) was shaken in an atmosphere of hydrogen when 1.5-2ml. were absorbed. On adding 9-phenylethylidenefluorene (0.53g.) dissolved in minimum ethanol, 38.5ml., of hydrogen were absorbed in 3 minutes. The reaction was stopped after 10 minutes when 52.5ml., hydrogen had been absorbed. The theoretical amount is 44ml., hydrogen at atmospheric pressure.

The catalyst was filtered off, the ethanol evaporated, the residue taken up in benzene and chromatographed through a short plug of alumina. On removing the benzene eluate, the resultant oil crystallised after several days from ethanol as colourless prisms.

m.p. 38-39°.

Yield: 0.48g. (90%).

Analysis: $C_{21}H_{18}$ requires C: 93.3% H: 6.7%

found C: 93.4% H: 6.6%

UV Spectrum:

9-Phenylethyl-fluorene	210.5(4.68)229.5(3.88)263.5(4.25) 267.3(4.25)291.0(3.76)300.5(3.94)
Fluorene	210.0(4.45)232.0(3.60)262.0(4.25) 289.0(3.80)300.0(4.00)
9-Methyl-fluorene	262.0(4.20)289.0(3.65)301.0(3.90)

(b) β-Phenylethyl bromide (4.5g., 0.024 moles) in dry ether (10ml.) was slowly added with stirring to an ethereal solution of 9-lithiofluorene prepared from fluorene (4g., 0.024 moles) and phenyl lithium (0.024g.) as described on page 150. There was a marked exothermic reaction, and the clear reddish-orange solution became cloudy green in appearance. Stirring was continued for half-an-hour, before the mixture was poured into water (50ml.), the ether layer separated, washed with water, and evaporated to give an oil.

Chromatography.

The column was made up of alumina (300 g.) in light-petroleum and the oil introduced in the minimum quantity of light-petroleum. The column was developed by eluting with light-petroleum gradually introducing benzene into the eluent by 5% increments.

Two products were obtained from the column in the following order:-

(i) Unchanged fluorene. 1.3g.

(ii) 9-β-Phenylethylfluorene. This was obtained initially as an oil, which, due to the low melting-point of the substance was extremely difficult to crystallise. The substance finally crystallised after trituration with ethanol and standing several days.

m.p. 38-39°. A mixed melting-point with the sample obtained above showed no depression.

Yield: 4.5g. (70%).

This compound proved to be unstable, slowly becoming an oil on standing.

Fluoren-9-ol-9-carboxylic acid (53).

Ethyl fluorene-9-carboxylate (2.38g.) was dissolved in toluene (12ml.) which was then distilled until 3ml. had been collected thus removing any trace of water from the solution. Sodium hydride (0.5g., 50% oil suspension) was added to this solution with stirring. The solution became green and the temperature rose - evidence of sodioderivative formation. β-Phenylethylbromide (1.85g.) was added with stirring and after ca. an hour the green colour had disappeared and a white precipitate settled out. The solution was refluxed for 3 hours, after which the solid was filtered off. Concentration of the filtrate gave an oil which could not be crystallised.

The solid material was dissolved in water and acidified with concentrated hydrochloric acid, crystals separating out. Re-crystallisation from benzene gave white needles.

m.p. 167-169°. (Lit. m.p. 167-169°).

Yield: 1.7g. (70%).

IR Spectrum: 3410 cm^{-1}. (m) (OH).

1715 cm^{-1}. (s) (C=O).

This material was decarboxylated by boiling with ethanolic potassium hydroxide. Removal of the ethanol, acidification and ether extraction etc., gave fluoren-9-ol, as white plates from benzene.
m.p. 152-154°, not depressed when mixed with an authentic sample.

Reduction of 9-phenacylfluorene.

(i) Huang-Minlon Modification.

9-Phenacylfluorene (1.4g., 5 m.moles), excess hydrazine hydrate, potassium hydroxide (0.6g., 10.5 m.moles) and diethylene glycol (15ml.) were heated at 200° in an oil bath for 3-4 hours, when the solution was clear red-purple in appearance. In the condenser there was fine white material which had slowly accumulated by sublimation during the time of heating. This material was shown by mixed melting-point to be fluorene.

Addition of water to the above red solution, followed by ether extraction, drying and evaporation gave an oil, which, after chromatography through alumina gave more fluorene. Total fluorene obtained 0.3g. (37%).

A similar result was obtained when the above experiment was conducted under nitrogen, although the purple colour gradually disappeared during the heating.

A blank experiment similar to the ones above but omitting the hydrazine hydrate did not yield any fluorene.

9-Phenacylfluorene hydrazone.

9-Phenacylfluorene (1g.) was dissolved in boiling ethanol (20ml.) and hydrazine hydrate (5ml., 100%) added. This mixture was heated in an oil bath at 80°. After one hour, a further quantity of hydrazine hydrate (5ml.) was added and heating continued at the same temperature for a further 2½ hours. Evaporation to dryness under reduced pressure, gave an oil, which on dissolving in the minimum boiling ethanol, with scratching and cooling, gave clear prisms of 9-phenacylfluorene hydrazone.

m.p. 104-105°

Yield: 0.5g. (49%).

Analysis: $C_{21}H_{18}N_2$ requires N: 9.34%

found N: 9.39%

IR Spectrum: No carbonyl absorption.

Reduction of 9-phenacylfluorene hydrazone.

To 9-phenacylfluorene hydrazone (0.5g., 1.7 m.moles) and dry potassium tert-butoxide (0.3g., 2.7 m.moles) was added 17ml. sulphur-free toluene, when the solution became pale red and red solid separated. Immediately on refluxing the solution became dark. Refluxing was continued for 4 hours, when a dark purple solution was obtained. After cooling and addition of water, the aqueous and toluene layers were separated, the aqueous layer being extracted with ether, and the two organic extracts combined, dried, and evaporated

to give an oil. Chromatography through alumina, eluting with 1:1 benzene light-petroleum gradually increasing to elution with pure benzene, gave two products.

(a) First off the column was spiro-1-(2-fluorenyl)2-phenylcyclopropane identified by mixed melting-point with an authentic sample.

Yield: 0.15 g. (54%).

(b) 9-Phenacylfluorene azine, also identified by mixed melting-point with an authentic sample.

Yield: 0.18 g. (32%).

(ii) 9-(2-Hydroxy-2-phenyl)ethylfluorene (29).

9-Phenacylfluorene (1g.) dissolved in the minimum ethanol was shaken with palladium-charcoal (0.1g.) in an atmosphere of hydrogen. Evaporation of the ethanol gave white crystals, m.p. 102-103°, a mixed melting-point with an authentic sample of 29 showing no depression.

Yield: 0.8 g. (80%).

BIBLIOGRAPHY

1. Campbell and Reid: J.C.S., 3281 (1952).
2. Clar: "Polycyclic Hydrocarbons", Vol.2., 335 (1964).
3. Berthelot: Ann. chim., (4), 12, 222 (1867).
4. Barbier: Ann. chim. phys., (5), 7, 472 (1876).
5. Fittig and Schmitz: Ann., 193, 134 (1878).
6. Burns and Iball: Nature, 173, 634 (1954).
7. Brown and Bortner: Acta. Cryst., 7, 139 (1954).
8. Cook and Iball: Chem. and Ind., 55, 467 (1936).
9. Cook et al: J.C.S., 1322 (1935).
10. Swain and Todd: J.C.S., 674 (1941).
    Bergmann and Szmuszkovicz: J.A.C.S., 75, 353 (1953).
11. Adam: Compt. rend., 103, 207 (1886).
12. Vorlander: Ber., 44, 2467 (1911).
13. Stoughton and Adams: J.A.C.S., 54, 4434 (1932).
14. Moore and Huntress: J.A.C.S., 49, 1324 (1927).
15. Schmidt et al: Ber., 38, 3737 (1905); 41, 3697 (1908).
16. Miller and Bachmann: J.A.C.S., 57, 2443 (1935).
17. Fittig et al: Ber., 10, 2141 (1877);
    Ann., 200, 1 (1879).
18. Sawicki, Chastain and Bryant: J. Org. Chem., 21, 754 (1956).
19. Rieveschl and Ray: Chem. Revs., 23, 287 (1937).
20. Sieglitz: Ber., 53, 1232 (1920).
21. Loevenich and Loeser: J. pr. Chem., 116, (ii), 325 (1927).

22. Streitwieser: "Molecular Orbital Theory for Organic Chemists", Wiley, p.44.

23. McEwen: J.A.C.S., 58, 1124 (1936).

24. Greenhow et al: J.C.S., 2848 (1951).

25. Weissgerber: Ber., 34, 1659 (1901).

26. Gilman: Org. Reactions, 8, 258.

27. Tucker and Whalley: J.C.S., 50 (1949).

28. de la Harpe and van Dorpe: Ber., 8, 1048 (1875).

29. Sampey and Reid: J.A.C.S., 69, 234 (1947)

30. Wittig and Felletschim: Ann., 555, 133 (1943).

31. Thiele: Ann., 347, 290 (1906);
Ber., 33, 851 (1900).

32. Schultz and Smullin: J.A.C.S., 62, 2904 (1940).

33. France, Maitland and Tucker: J.C.S., 1739 (1937).

34. Brunson: J.A.C.S., 64, 2457 (1942).

35. Campbell and Fairfull: J.C.S., 1239 (1949).

36. Von and Wagner: J. Org. Chem., 9, 155 (1944).

37. Tucker: J.C.S., 2182 (1949).

38. Wislicenus and Russ: Ber., 43, 2719 (1910).

39. Kuhn and Levy: Ber., 61, 2240 (1928).

40. Wawzonek and Defek: J.A.C.S., 78, 3530 (1956).

41. Kuhn et al: Ann., 654, 64 (1962).

42. Kruber: Ber., 67, 1000 (1934).

43. Bachmann and Sheehan: J.A.C.S., 63, 204 (1941).

44. Medenwald: Ber., 86, 287 (1953).

45. Reid: Ph.D. Thesis, p.108, Edinburgh (1951).

46. Freudenberg and Blümmel: Ann, 440, 51 (1924).

47. Reid: Ph.D. Thesis, p.110, Edinburgh (1951).

48. Swan: Ph.D. Thesis, p.25, Edinburgh (1952).

49. Goldschmiedt: Ber., 10, 2022 (1877)

50. von Braun and Anton: Ber., 62, 145 (1929).

51. Tucker: J.C.S., 803 (1952).

52. Campbell and Wang: J.C.S., 1513 (1949).

53. Bergmann and Orchin: J.A.C.S., 71, 1917 (1949).

54. Tucker et al: J.C.S., 1137 (1948); 632, 3213 (1949); 3286 (1950).

55. Bergmann and Orchin: Nature, 161, 889 (1948).

56. Deno: J.A.C.S., 72, 4057 (1950).

57. Kloetzel and Mertel: J.A.C.S., 72, 4786 (1950).

58. Campbell and Gow: J.C.S., 1555 (1949); Nature, 162, 857 (1948).

59. Tucker and Campbell: J.C.S., 2623 (1949).

60. Kruber and Grigoleit: Ber., 87, 1895 (1954).

61. Wynder et al: a). Cancer, 12, 1194 (1959); b). Cancer, 15, 79 (1962).

62. Badger and Novotny: Australian J. Chem., 16, 613 (1963).

63. Ehrlich and Beevers: Acta. Cryst., 9, 602 (1956).

64. Swan: Ph.D. Thesis, p.41, Edinburgh (1952).

65. Reid: Ph.D. Thesis, p.136, Edinburgh (1951).

66. Swan: Ph.D. Thesis, Edinburgh (1952).

67. Foggo: Ph.D. Thesis, Edinburgh (1954).

68. Caglioti and Grasselli: Chem. and Ind., 42, 153 (1964).

69. Parker: Quart. Revs., 16, 163 (1962).

70. Kurtz: Methoden der Org. Chemie., III, 294.

71. Price and Oae: "Sulphur Bonding", Ronald Press, p.134.

72. Bayer: Methoden der Org. Chemie, II, 193.

73. Eaton and Cole: J.A.C.S., 86, 962 (1964).

74. Geuther: Gottinger Anzeigen, 281 (1863);
Arch. Pharm., 106, 97 (1863);
Jahresber, 323 (1863).

75. Butlerow: Ann., 189, 44 (1877).

76. Baeyer: Ber., 15, 2093 (1882); 16, 2188 (1883).

77. Laar: Ber., 18, 648 (1885); 19, 730 (1885).

78. Claisen: Ann., 291, 25 (1896).

79. Knorr: Ann., 293, 70 (1896); 306, 322 (1899).

80. Wislicenus: Ann., 291, 147 (1896); 312, 34 (1900);
Ber., 32, 2837 (1899).

81. Hantzsch: Ber., 29, 699, 2251 (1896).

82. Knorr: Ber., 44, 1138 (1911).

83. Knorr: Ann., 293, 38 (1896).

84. Wislicenus: "Uber Tautomerie", 2, 187 (1898);
Ingold: "Structure and Mechanism in Organic Chemistry", p.543.

85. Ingold and Piggott: J.C.S., 121, 2381 (1922).

86. Griess: Ber., 7, 1618 (1874);
Ann., 137, 60 (1886).

87. Pechmann: Ber., 28, 869, 2362 (1895); 30, 1779 (1897).

88. Marckwald: Ann., 286, 343 (1895).

89. Wheeler and Johnson: Ber., 32, 35 (1899);
Roberts: J.A.C.S., 72, 3603 (1950).

90. Ingold and Shoppee: J.C.S., 447 (1929).

91. Shoppee: J.C.S., 968 (1930); 1225 (1931); 696 (1932).

92. Ingold and Rothstein: J.C.S., 1666 (1931).

93. Craig: Ph.D. Thesis, p.61, Edinburgh (1955).

94. Elderfield and King: J.A.C.S., 76, 5439 (1954).

95. Ashley: J.C.S., 115 (1942).

96. Kon and Linstead: reviews of their work by:-

Baker: "Tautomerism", Chapt., 9, Routledge (1934).

97. de la Mare, Hughes, and Ingold: J.C.S., 22 (1948).

98. Campbell et al: J.C.S., 781 (1960).

99. Ingold: Ann. Reports, 24, 106 (1927).

100. Baker: "Tautomerism", Chapt., 6, Routledge (1934).

101. Baker: "Tautomerism", p.86, Routledge (1934).

102. Wislicenus and Waldmuller: Ber., 42, 785 (1909).

103. Schlenk and Bergmann: Ann., 463, 271 (1928).

104. Pandya and Pandya: J. Chem. Ed., 28, 46 (1951).

105. Clar: "Polycyclic Hydrocarbons", Vol. 2, p.336, (1964).

106. Koelsch and Johnson: J. Org. Clem., 6, 538.(1941).

107. Burckhalter and Johnson: J.A.C.S., 73, 4832 (1951).

108. Burns and Iball: Proc. Roy. Soc., A.227, 200 (1954).

109. Fenimore: Acta. Cryst., 1, 295 (1948).

110. Craig: Ph.D. Thesis, pp.40, 109, Edinburgh (1955).

111. Rutovskii and Zabrodina: J. Applied Chem. (U.S.S.R.), 11, 302. cf. Chem. Abs., 32: 5777^{9}.

112. McKenna, Tartar and Lingafelter: J.A.C.S., 71, 729 (1949); 75, 604 (1953).

113. Ashdown and Kletz: J.C.S., 1454 (1948).

114. Wadsworth and Emmons: J.A.C.S., 83, 1733 (1961).

115. Beech, Turnbull and Wilson: J.C.S., 4686 (1952);
Lardelli and Jeger: Helv. Chim. Acta., 32, 1817 (1949).

116. Huang - Minlon: J.A.C.S., 68, 2487 (1948).

117. Bamford and Stevens: J.C.S., 4735 (1952).

118. Meinwald et al: J. Org. Chem., 29, 3469 (1964).

119. Krapcho and Diamanti: Chem. and Ind., 847 (1965).

120. Hurd and Cohen: J.A.C.S., 53, 1068 (1931).

121. Bethell and Cockerill: Proc. Chem. Soc., 283 (1964).

122. Gilman: J. Org. Chem., 1, 315 (1936).

123. Fuson and Mumford: J. Org. Chem., 17, 255 (1952).

124. Grundon and Henbest: J.C.S., 1855 (1963).

125. Wislicenus and Mocker: Ber., 46, 2792 (1913).

126. Cowper and Davidson: Org. Syn., 19, 24.

127. Garden and Gunstone: J.C.S., 2650 (1952).

128. de Boer and Backer: Rect. Trav. Chim., 73, 229 (1954).

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